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# THE AMERICAN MINERALOGIST

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## THERMAL STUDY OF THE Ca-Mg-Fe CARBONATE MINERALS\*

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### ABSTRACT

Differential thermal analyses have been made of a large number of natural carbonate minerals in the Ca-Fe-Mg composition triangle. The characteristics of the thermal behaviour of these minerals and the related structural changes have been investigated and defined. X-ray diffraction and chemical analysis were used to identify structural phases and substitution phenomena in the group. Substitution in calcite, magnesite, siderite, dolomite, and ankerite is readily detected by thermal studies. It is possible to quantitatively estimate the concentrations of each of these common carbonate minerals in a natural aggregate and to estimate the amount of substitution in each phase. Evidence for complete ionic substitution between the pairs Ca-Mn, and Fe-Mg, now seems clear. Between Ca-Mg and Ca-Fe, however, the amount of substitution in a calcite type lattice is very limited. Complete substitution between Fe and Mn, and between Mg and Mn appears possible but is not completely represented in minerals.

### I. INTRODUCTION

The carbonates of calcium, magnesium, and ferrous iron occur under various geologic conditions. While the atomic architecture of the minerals which these cations form has been known for some time (Bragg, 1937), these studies were only concerned with the relatively pure single crystals. The natural occurrence of carbonate aggregates is often highly complex. Differential thermal analysis (DTA) appeared to offer a means of

\* Contribution No. 37, Lamont Geological Observatory.



defining the fraction of each mineral lattice present in such mixtures and the concentration of each cation in each lattice. The correlation of the thermal data with the structural pattern should provide a broader understanding of these minerals in their natural occurrence. In addition, these data may contribute to a better understanding of such widely different occurrences as the siderite iron ores, carbonate mineralization associated with hydrothermal deposits and petroliferous sediments.

The focus of this study lies in the ankerite area of the Ca-Fe-Mg composition triangle. In order to adequately interpret the data on ankerite, it was desirable to do some preliminary work on the simple carbonates. Some of these minerals have been described in the DTA literature. Beck (1950), Cuthbert and Rowland (1947), and Kerr and Kulp (1948) have made reconnaissance DTA studies on one or two specimens of various common carbonates. Fredrickson (1948), Rowland and Jonas (1949), and Kerr and Kulp (1947) have published more detailed work on siderite. Faust (1950) has done a careful study of calcite and aragonite and has published some thermal work on dolomite and magnesite (Faust, 1944, 1949). Kulp, Wright, and Holmes (1949) made a thermal study of the closely related rhodochrosite and the substitution phenomena from rhodochrosite to calcite. No extensive DTA work has appeared on ankerite or the synthesis of the thermal relationships in the common carbonates.

The authors wish to acknowledge the assistance of H. Adler, H. Glass, and P. K. Hamilton in the experimental work. They are particularly grateful to Mr. Franz Dykestra and the H. A. Brassert Co. who supplied many chemically analyzed siderite-ankerite ore specimens.

## II. EXPERIMENTAL PROCEDURE

The differential thermal analysis equipment used in this study is described in two papers (Kerr and Kulp, 1948; Kulp and Kerr, 1949). The 1948 paper includes a discussion of the theoretical heat relationships.

The ground sample (80–220 mesh) is packed into a cylindrical well which contains one terminal of a two-headed thermocouple. The other terminal is placed in some material, such as alundum, which does not undergo exothermic or endothermic reactions through the heating range. The temperature of the system is then raised at a uniform rate from room temperature to 1050° C. Any thermal changes in the sample well will result in a differential temperature between the two terminals. This is measured by a recording potentiometer in a plot of time or system temperature against differential temperature. The area under a peak on such a curve is proportional to the heat of reaction and concentration of the active ingredients.



In order to make the curve from successive runs and in different wells comparable, the system is calibrated for sensitivity by taking thermal curves of standard kaolinite in each well every few runs. Further, all curves in this study were run in duplicate.

In addition to the DTA curves for all specimens, many of the more interesting or typical specimens were subjected to *x*-ray diffraction for purposes of phase identification. The high and low indices were determined to  $\pm 0.005$  for a large fraction of the specimens to check trends in the optical properties with composition and thermal behaviour.

Some chemical data were available for most of the specimens. Eleven of the more typical samples from the Columbia University Mineralogy Collection were analyzed for the common cations and carbon dioxide by Ledoux and Co., New York. H. A. Brassert and Co. supplied complete chemical analyses on nine specimens and partial analyses on thirty two others. In order to interpret the thermal curves of the other specimens they were quickly analyzed for Ca, Fe and Mg by a semi-micro scheme in which known control samples were used. This effectively raised a qualitative method to a semi-quantitative method. The concentration of the three cations in the cation position could be estimated by this method to about  $\pm 10\%$ .

### III. EFFECTS OF PARTICLE SIZE AND DILUENT

It has been shown by many workers that the peak temperature is affected both by the particle and crystallite size as well as the concentration. In the carbonate minerals these effects are particularly marked due to the large peaks, the wide range in particle size in natural occurrences, and the asymmetry of the peaks. In order to interpret the thermal curves of natural carbonate aggregates, it is necessary to have some notion of the amount of temperature shift. These have been established for most of the minerals discussed in this paper but it will suffice for illustrative purposes to discuss only calcite. The paper by Rowland and Jonas (1949) shows the effects for siderite.

Figure 1 shows the particle size effect with calcite. A specimen of Iceland spar from Santa Fe, New Mexico, was crushed and separated into size groups from 50 to 200 mesh. Some of the 200 mesh material was further ground in an agate mortar until the powder was extremely fine (*x*-ray size). In order to obtain the curve of very fine calcium carbonate, some was freshly precipitated from a calcium nitrate solution at room temperature. It appears that the particle size does not affect the curve appreciably down to 200 mesh. For the very fine carbonate particles the temperature is shifted downward. Sedimentary carbonate is usually fine grained but hydrothermal-metamorphic carbonate is more



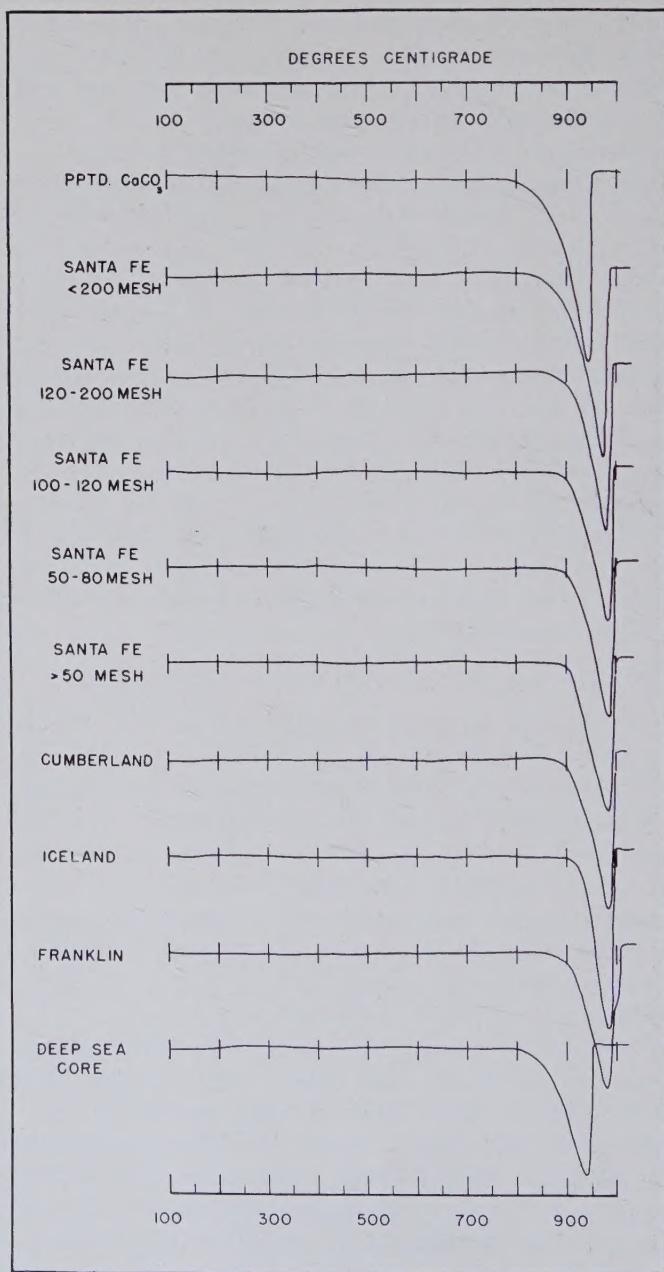


FIG. 1. DTA curves of various specimens of calcite and of various particle sizes for the Santa Fe-Iceland spar.



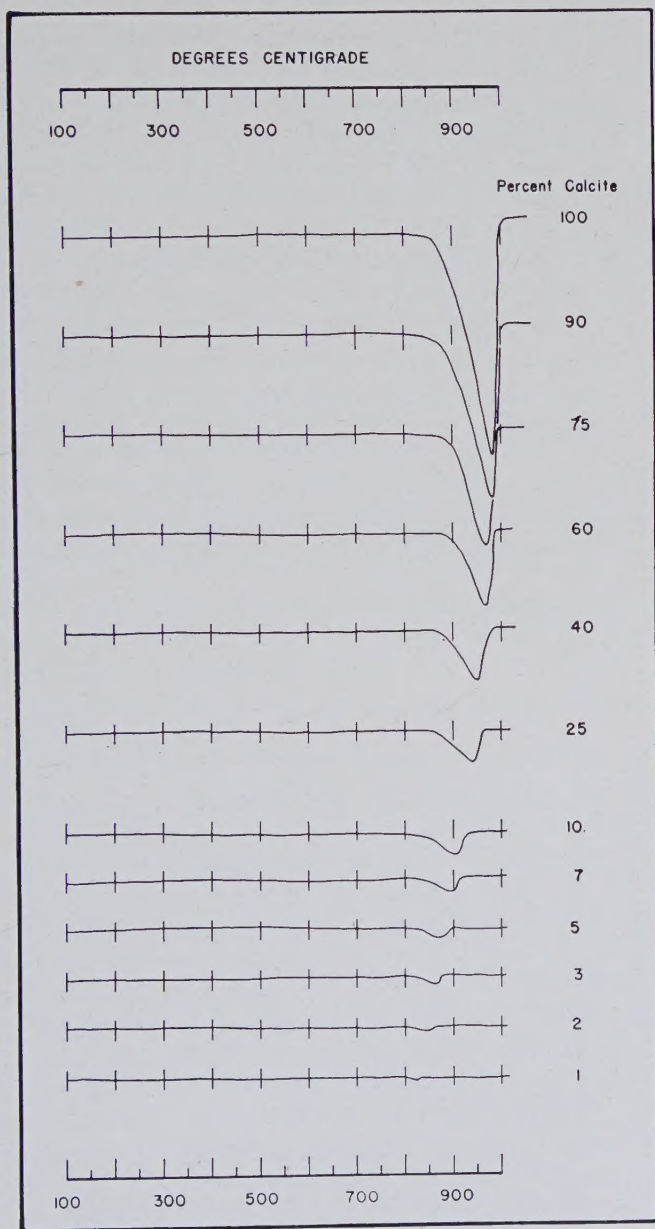


FIG. 2. DTA curves of calcite-alundum mixtures. The calcite is Iceland spar ground to 120-200 mesh.



likely to be rather coarse in texture. It appears that both the peak temperature and the initial decomposition temperature decrease with particle size. The peak temperatures may drop from  $980^{\circ}\text{C}$  to  $930^{\circ}\text{C}$  due to this effect. It is interesting to note, however, that the asymmetry of the curve is not disturbed by a shift in peak temperature. It can be safely assumed that the other carbonates show similar particle size effects. The Cumberland, Iceland, and Franklin calcite specimens are all coarsely crystalline. Only in the case of those carbonates which contain oxidizable ions must this simple picture be modified. In this case the decrease in initial decomposition temperature with particle size follows that of calcite, but the peak temperature may be modified by the ease of oxidation and hence the start of the exothermic reaction.

Figure 2 shows curves of Iceland spar ground to 120–200 mesh and mixed with alundum. The curves show the effects resulting from an inert impurity. The peak temperature is decreased from  $980^{\circ}\text{C}$  to  $820^{\circ}\text{C}$ . The shape of the curve changes considerably, but the initial decomposition temperature does not vary greatly until rather low concentrations are reached. Since this set of curves was obtained with the

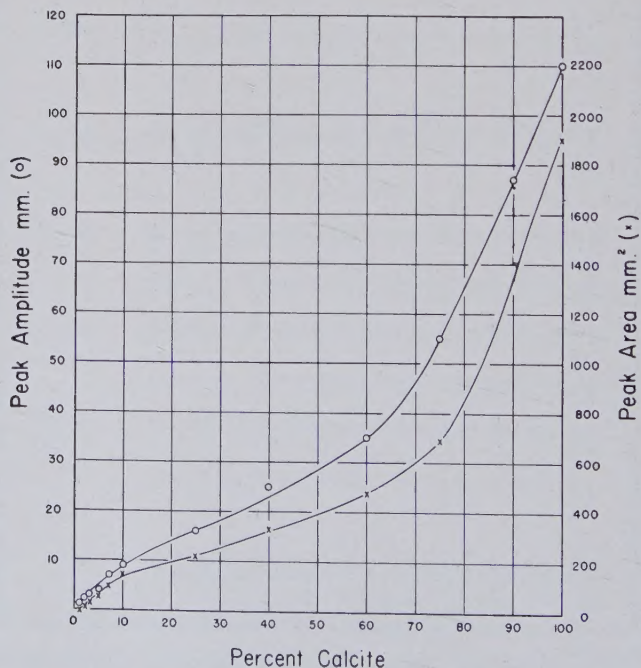


FIG. 2a. Peak area and amplitude against concentration for coarse calcite-alundum mixtures.



coarse calcite, it would seem that the combination of very fine particle size and low concentration might produce calcite peaks as low as 800° C. The characteristic asymmetry of the calcite peak assists in identifying the mineral in low concentrations.

Figure 2a shows the data of Fig. 2 plotted for use as a calibration curve for quantitative estimation. It is apparent that either peak area or peak amplitude may be used as a concentration index providing conditions are equivalent in the calibration sample and the unknown. However, the area remains relatively constant with changing particle size while the amplitude varies; hence the area is to be preferred practically. Theoretical considerations (Kerr and Kulp, 1948) agree that this should be the case.

#### IV. DTA OF CA-MG-Fe CARBONATE MINERALS

The minerals studied include calcite, siderite, magnesite, dolomite, ankerite, and natural mixtures of these. Figure 3 shows the "ideal" DTA curves for these minerals as obtained from this study. For these "ideal" curves it is assumed that the samples are coarsely crystalline, chemically pure and have been run in a thermal analysis unit of the type described by Kerr and Kulp (1948). The shapes of the oxidation peaks are not as readily reproducible even with a fixed experimental arrangement as the other peaks.

##### *A. Calcite*

The general features of the DTA curves of calcium carbonate have been suggested by several workers, but Faust (1950) was the first to publish a detailed study of the thermal properties of aragonite and calcite. DTA curves of calcite from various localities have been included in this report to complete the group. Figure 1 shows the curves of five calcite specimens. Clear coarse calcite from Iceland gives the sharpest peak. The sample from Franklin may be a mixture of two calcites of different crystallite size. Faust (1950) observed subsidiary breaks on the high temperature side of the peak in samples which were mixtures of calcite and aragonite. This was attributed to different decomposition temperatures for the primary calcite and the calcite produced from the aragonite transformation at 400–450° C. Since the peak characteristic of this transformation does not appear in the thermal curve of the Franklin sample, it is likely that two calcites are present rather than a mixture of aragonite and calcite. An x-ray pattern of this sample confirmed the absence of aragonite.

All calcite curves show an elevation of the base line after the decomposition due to the difference in specific heat of calcite and CaO. The

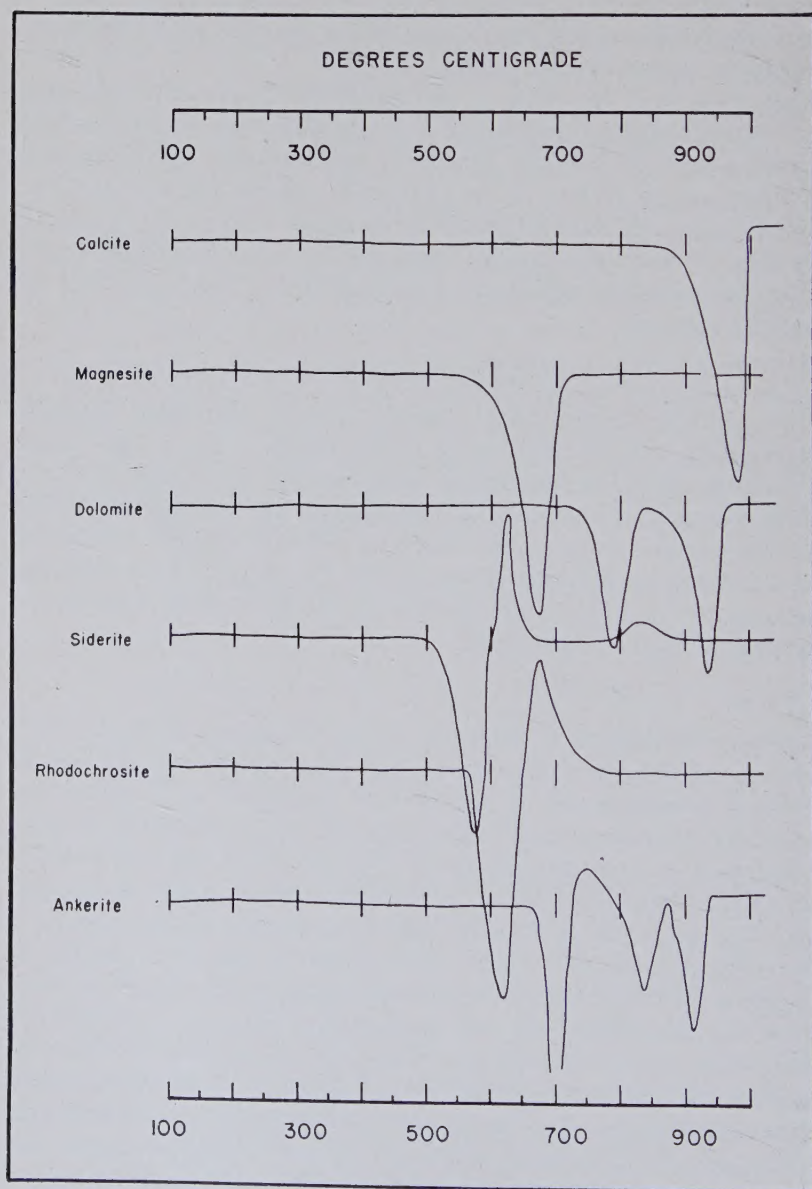


FIG. 3. Theoretical DTA curves for pure carbonate mineral mixtures.



deep sea calcite taken from an Eocene core in the North Atlantic shows a lower peak temperature as expected for the very fine particle size. The broad peaks sometimes observed on natural calcite aggregates indicate a wide spread of particle size.

### *B. Siderite*

There are a number of published DTA curves of siderite (Cuthbert and Rowland, 1947) (Kerr and Kulp, 1947) and (Fredrickson, 1948). Rowland and Jonas (1949) have contributed considerably to the knowledge of the thermal behaviour of siderite. They were particularly concerned with the interpretation of the variation in the peaks due to rates of oxidation.

If a specimen of siderite of the ideal composition is thermally analyzed in air without dilution by an inert substance, a curve such as that shown in Figure 3 will result. The exact shape of the exothermic peak will be dependent on the tightness of packing, size and shape of the sample well, and particle size. The endothermic peak represents the decomposition of siderite to FeO. This is oxidized to  $\text{Fe}_2\text{O}_3$  giving the major exothermic peak. The product after the first exothermic peak is a mixture of hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ). The proportion of these polymorphs is determined by the rate of oxidation and the degree of substitution in the siderite lattice. Apparently oxygen catalyzes the transformation to  $\alpha\text{-Fe}_2\text{O}_3$  for the more open sample, the more  $\alpha\text{-Fe}_2\text{O}_3$  formed. This is to be expected since maghemite is essentially a spinel lattice with defects. Apparently magnetite does not form under these conditions. The second exothermic peak is due to the transformation of  $\gamma\text{-Fe}_2\text{O}_3$  to  $\alpha\text{-Fe}_2\text{O}_3$ . The material at  $1000^\circ\text{C}$  is essentially hematite. X-ray patterns of samples, which were heated to various temperatures in this work, confirm the data and interpretation of Rowland and Jonas (1949). Beck (1950) failed to mention the second endothermic peak and its significance even though it is apparent in the thermal curve of a specimen labelled "Saxony."

Figures 4 and 5 show the DTA curves of some representative siderite specimens which permit a number of general conclusions to be drawn. If the specimen is so coarsely crystalline that all of the crystal grains are larger than the ultimate mesh size after crushing, a sharp peak such as that obtained in 4-10, 5-6, or 5-11 is obtained. A relatively broad endothermic peak such as 4-8 or 5-1 is indicative of a wide range in crystallite size. The initial decomposition temperature, which in these curves ranges from 5-1 ( $380^\circ\text{C}$ ) to 4-12 ( $600^\circ\text{C}$ ), is dependent on both crystallite size and substitution of  $\text{Mn}^{++}$  and  $\text{Mg}^{++}$  for  $\text{Fe}^{++}$ . A gradual deviation from the base line such as 4-8 or 5-1 compared to a sharp break as in 4-10

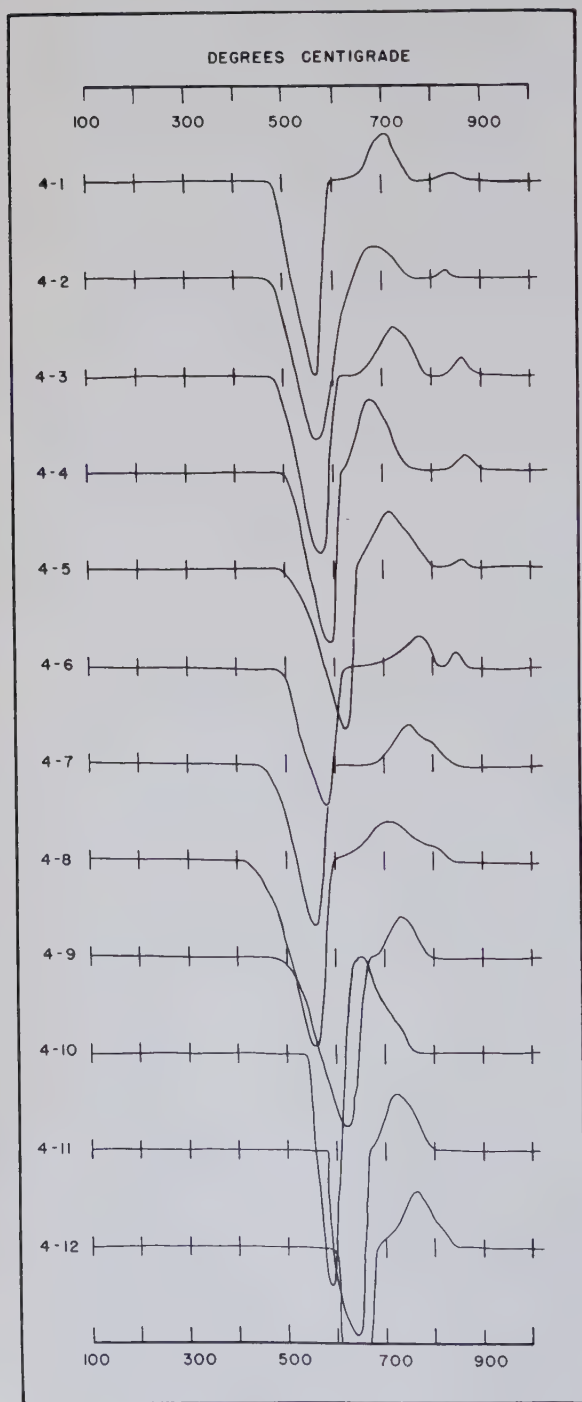


FIG. 4. DTA curves of selected siderite specimens:

- 4-1 Waldstein, Carinthia
- 4-2 Roxbury, Conn. (1)
- 4-3 Andreasburg, England
- 4-4 Roxbury, Conn. (2)
- 4-5 Porco, Bolivia
- 4-6 Přeborn, Bohemia
- 4-7 Devonshire, England
- 4-8 Cornwall, England
- 4-9 Dauphine, France
- 4-10 Neudorf, Germany
- 4-11 Traversella (1), Italy
- 4-12 Germany



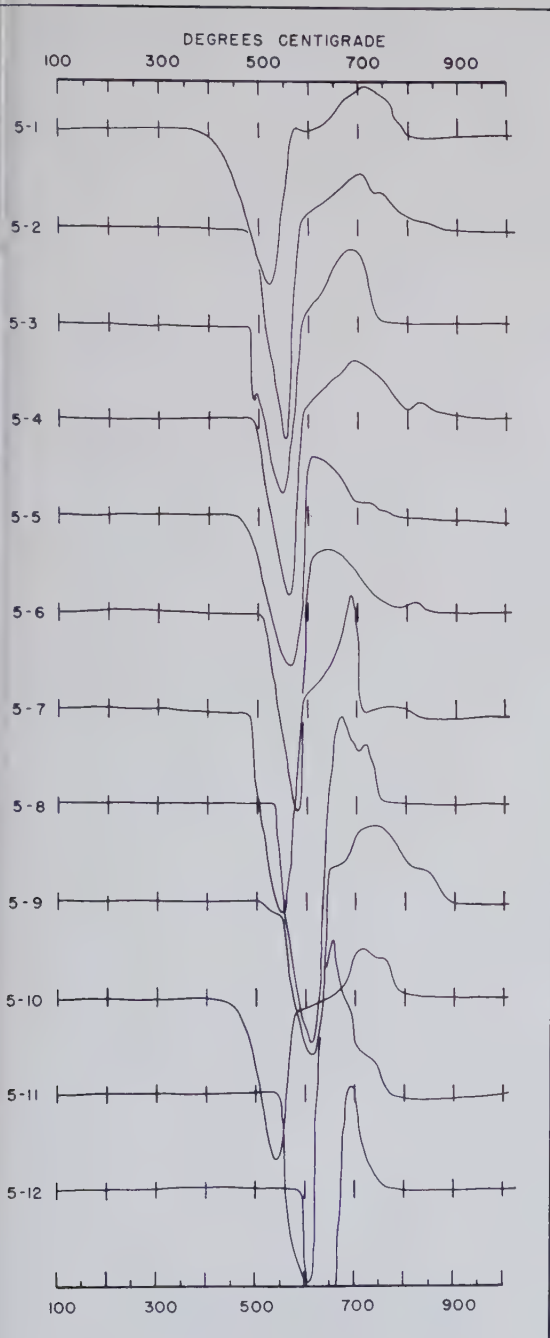


FIG. 5. DTA curves of selected siderite specimens:

- 5- 1 Redrush, Cornwall (1)
- 5- 2 REO 6A (Styria)
- 5- 3 Danville, Pa.
- 5- 4 KLE 2B (Styria)
- 5- 5 Crassbackel (Styria)
- 5- 6 KLE 2A (Styria)
- 5- 7 Westphalia, Germany
- 5- 8 Mines de Allerd, France
- 5- 9 Galpina Co., Calif.
- 5-10 Missouri
- 5-11 Rutland, Vt.
- 5-12 Brazil (2)

or 4-11 indicates a range in particle size. In the latter case, particle size is probably quite important in determining the peak temperature.

Most natural siderite specimens contain a few per cent MnO. Usually this is not enough to shift the peak temperature since even pure rhodochrosite has an endothermic peak temperature of only 620–630° C (Kulp, Wright and Holmes, 1949). The average endothermic peak temperature for reasonably pure coarse siderite is near 550° C. Beck (1950) shows a DTA curve of a siderite with 17% MnCO<sub>3</sub> with the endothermic peak near 580° C. Samples 5-2, 5-4, and 5-6 had only 2% MnO present so the higher temp. of 5-6 must be attributed to Mg or Ca substitution. Semi-quantitative analysis shows 5-6 to contain considerable Mg (20 ± 5% cation positions) but insignificant Ca. That the Mg is more important than Mn in raising the peak temperature is expected since the decomposition temp. of magnesite is 700° C. Chemical analysis of the Roxbury sample (4-4) which gave a peak at 570° C was 4.10% MgO while the Dauphine specimen (4-9) gave a peak at 600° C and contained 13.07% MgO. While quantitative chemical analyses were not available for the other samples, semi-quantitative analysis showed that all the specimens with high peak temperature such as 4-5, 4-10, 4-11, 4-12, 5-8, 5-9, 5-11, 5-12 to be high in magnesium, while 4-1, 4-2, 4-7, 4-8, 5-1, 5-2, 5-3, 5-4, 5-5, 5-7, and 5-10 were low in MgO content.

The areas under the endothermic peaks vary more in the case of siderite than calcite because the exothermic reaction is so intimately tied to the endothermic reaction. For careful quantitative work with siderite in natural aggregates, it is necessary to work in an inert atmosphere so that the readily reproducible endothermic peak could be studied alone.

The variations in the exothermic peaks require further study but some features may be defined. The second exothermic peak appears to vary both in peak temperature and amplitude. Since the concentration and distribution of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> depends on the rate of oxidation, the extent of substitution and the presence of impurities, it is expected that neither the concentration of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nor the temperature of transformation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is constant. For the most typical siderite specimens in which substitution is unimportant, the second exothermic peak appears between 830 and 860° C as in 4-1, 4-2, 4-3, 4-4, 4-5, 4-6, 5-4, and 5-6. Occasionally this peak may occur at a lower temperature and may be blended into the first endothermic peak, particularly if the latter is delayed in its appearance. Such a relationship is suggested in curves 4-7, 4-8, 4-10, 5-1, 5-2, 5-5, 5-7, 5-9, 5-10, 5-11. All specimens in which the decomposition starts at 500° C or less show the two exothermic peaks. However, in the samples with the highest Mg content (4-9, 4-11, 4-12, and 5-12), which have endothermic peak temperatures in excess



of 600° C, the second exothermic peak appears insignificant. With high Mg content, therefore, the products are probably hematite and periclase. While it is possible that magnesioferrite ( $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ ) could form under these conditions, the evidence for its existence from  $x$ -ray diffraction patterns taken on material heated to 1000° C is inconclusive. In general the area under the exothermic peaks decreases with increased magnesium substitution. Compare, for example, 4-9 with 4-10. The low area and delayed peak temperature for 4-6 is due to the presence of clay material which prevented ready access of the air to the  $\text{FeO}$ .

The optical and  $x$ -ray data for these specimens of siderite proved consistent with the DTA curves and the chemical composition. On all samples with little substitution, the low index was 1.63 to 1.65 and the high index 1.86 to 1.88. The samples with 20% Mg in the cation positions gave a low index of 1.59 to 1.60 and a high index of 1.80 to 1.82. The indices for pure magnesite are low 1.52 and high 1.70. The data do not justify a plot since the index is affected by Ca and Mn substitution as well as Mg. An analogous relationship held for the "d" values calculated from powder patterns.

### C. Magnesite

The DTA of several magnesite curves has been reported in the literature. They are not all consistent. Faust (1949) shows a thermal curve of a magnesite listed as pure which shows an exothermic peak following the main endothermic peak. This is probably due to iron substitution in the lattice. Pure coarsely crystalline magnesite yields a simple endothermic peak at about 680–700° C. The reaction product is periclase, identified by  $x$ -ray diffraction.

Figure 6 shows the thermal curves of the selected magnesite specimens. The effect of particle size is present but to a less extent than in calcite. Specimens 6-8, 6-9, and 6-10 are visibly grained whereas the other specimens were microcrystalline. The initial decomposition temperature and the peak temperature are related to particle size. Chemical analysis of 6-1 shows 1.57% CaO and 1.14%  $\text{Fe}_2\text{O}_3$  with 46.12% MgO. If the calcium is present as calcite, even this small amount should show on the thermal curve (See Fig. 2). The quantity of iron is apparently insufficient to produce a visible exothermic reaction. Both Ca and Fe are therefore presumably substituted and roughly balance each other in effect on the peak temperature. It is thought that 6-1 is nearly representative of the ideal curve for magnesite. Semi-quantitative chemical analysis and optical examination indicate that 6-2 is quite similar to 6-1. The thermal curve indicates a slightly higher CaO concentration. 6-3 has less iron than 6-1 (semi-quantitative) but has 1–2% Ca. The DTA curve indi-

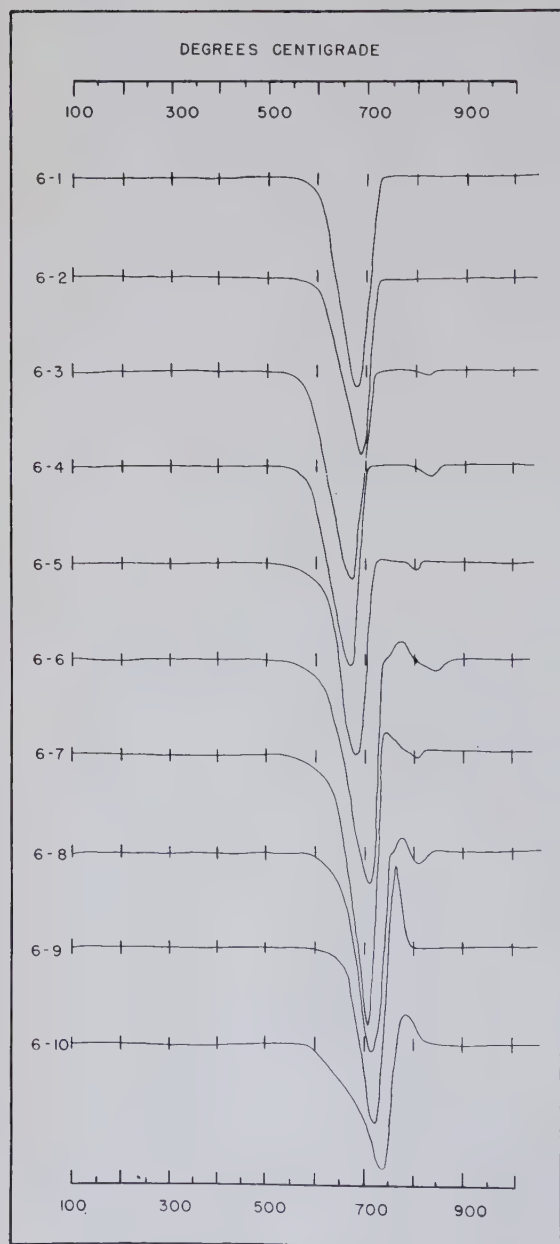


FIG. 6. DTA curves of representative magnesite specimens:

- 6- 1 Moravia, Czech.
- 6- 2 Baumgarten, Germany
- 6- 3 Halilona
- 6- 4 Brucite, Nevada
- 6- 5 Muntodi
- 6- 6 Hoboken, N. J.
- 6- 7 Eureka, Nevada
- 6- 8 Trieben
- 6- 9 Greiner, Austria
- 6-10 Chewelah, Wash.



cates this is present as calcite ( $820^{\circ}\text{C}$  peak). 6-4 and 6-5 are very similar to 6-3 but with slightly higher CaO content. In 6-5 it appears that some of the Ca is in the magnesite lattice due to the higher peak temperature despite the low initial decomposition temperature. 6-6 has more iron and calcium (est. 1-5% each) than 6-5. The substituted iron is sufficient to produce an exothermic peak and the calcium is distributed between substituted calcium and calcite (est. 5%). 6-7 is similar to 6-6 in composition but apparently the admixed calcite is of finer crystallite size. 6-8 from Trieben showed 2.00% CaO and 2.20%  $\text{Fe}_2\text{O}_3$  on analysis. It appears that roughly half of the calcium is present as calcite and half in the lattice. The higher peak temp. is related primarily to the particle size. The sample from Greiner (6-9) gave an analysis: CaO, 0.79%;  $\text{Fe}_2\text{O}_3$ , 11.37%. It was the coarsest magnesite studied. The peak size and shape is consistent with this physical and chemical data. 6-10 has a fairly coarse texture, is estimated to have 5%  $\text{Fe}_2\text{O}_3$  and may contain some inert impurities. The extreme asymmetry of the curve may indicate a mixture of siderite and magnesite, or two magnesites in which one generation contains most of the iron.

In general the optical data show both indices to be higher for the specimens containing more iron. Since these samples have three or four cation components (Ca, Fe, Mg, Mn), the optical data do not fall on a smooth curve from magnesite to siderite. They may be used, however, to indicate iron substitution providing the calcium content is not too high. The x-ray "d" values show the same trends.

#### *D. Dolomite-Ankerite*

It is reasonable to treat these minerals under one section because they are structurally identical and continuously related. "Dolomite" with less than 1%  $\text{Fe}_2\text{O}_3$  is rare and "ankerite" with a simple Mg:Fe ratio of 1:1 is uncommon. Ankerites have been found in this study in which the iron in the magnesium positions ranges from 5% to 70%.

Faust (1949) has published a curve for dolomite and Beck (1950) shows the curves of one dolomite and two ankerites. However, little has been recorded about the thermal-structural relationships of this important group of carbonates.

The structure of dolomite (Bragg 1937) does not consist of randomly substituted Mg ions in a calcite lattice but rather has two distinct cation positions, the smaller occupied by the Mg and the larger by the Ca. The two cations alternate in layers perpendicular to the *c*-axis. While examples of magnesian calcite have been cited, generally there is a distinct break between dolomite and calcite. The dolomite lattice provides a more stable way to pack equal quantities of Ca and Mg among carbonate

ions. From this picture of the lattice one would assume that the Fe ions would substitute primarily in the Mg positions. Actually this is found to be amazingly rigorous in the following data.

Figures 7 and 8 show the thermal curves of some representative dolomite-ankerite specimens. It is evident that dolomite, when sufficiently pure, such as 7-1, 7-2, and 7-3 yields two endothermic peaks while ankerite displays three. The peak shapes, amplitudes and positions depend on the crystallite size, degree of substitution, and the amount of mixing of different minerals of this group.

The first endothermic peak in either dolomite or ankerite is due to the decomposition of the carbonate ions most closely associated with the magnesium positions. The temperature at which this peak occurs depends on the particle size and iron substitution. The temperature at which the decomposition initiates is also determined by these factors. The sharpness of this peak is related to grain size primarily so this can be used to delineate the effects of particle size and substitution on the peak temperature. X-ray patterns of ankerites heated past the first endothermic peak are diffuse but indicate the presence of calcite, MgO and maghemite as separate phases even though they must be separated on a very fine scale. This fails to agree with Beck (1950) who stated that the first peak is due to the decomposition of iron carbonate only. No dolomite lines have been found in any of these specimens after heating past the first peak. Further, the size of the second endothermic peak increases continuously with increasing  $\text{Fe}^{++}$  content. Therefore, it can not be due to  $\text{MgCO}_3$  decomposition as Beck suggests.

The second endothermic peak in dolomite (7-1) and the third peak in ankerite remain fairly constant in temperature, shape and amplitude. Both are broadened and reduced in amplitude and temperature by inert impurities (8-9), and are somewhat affected by total iron content. This peak is due to the release of  $\text{CO}_2$  attached to the calcium ions.

The middle endothermic peak in ankerite has several interesting features. It increases in area with increase in iron concentration in Mg positions. Further, temperature of the peak is essentially independent of particle size or substitution.

The exothermic oxidation of  $\text{Fe}^{++}$  to  $\text{Fe}^{+++}$  after the initial decomposition is generally masked but in those samples of high iron content such as 7-8 and 7-10, the exothermic reaction is quite distinct.

Quantitative chemical analyses are available for a number of the specimens used in obtaining Figure 7. The other specimens in Figs. 7 and 8 were either partially analyzed quantitatively or semi-quantitatively. An evaluation of the thermal data in terms of these analyses is instructive. Table 1 shows the quantitative chemical data recomputed on a



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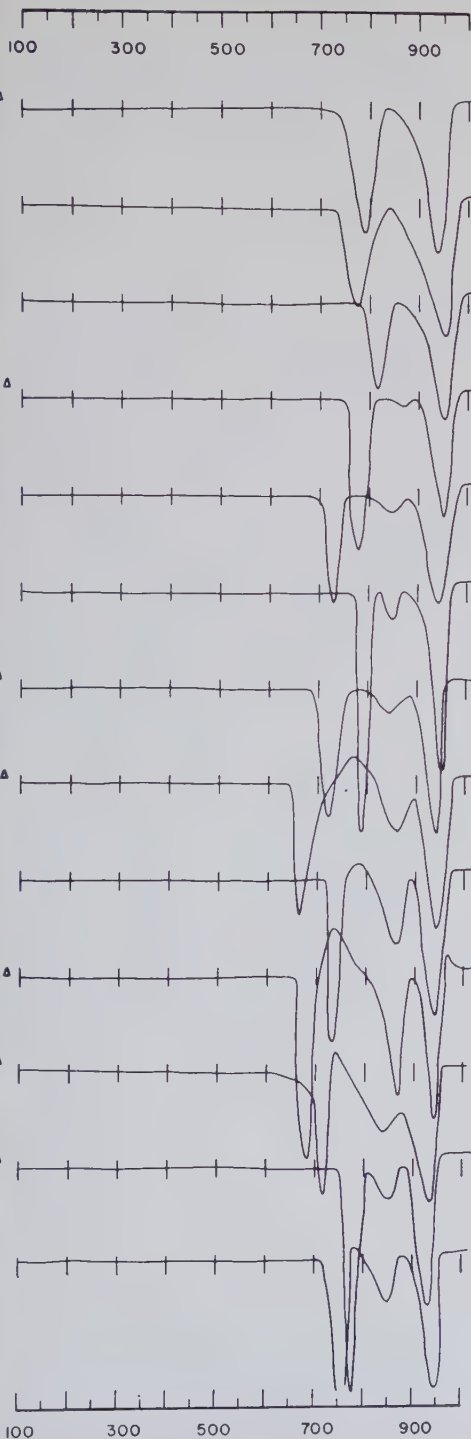


FIG. 7. DTA curves of selected dolomite and ankerite specimens:

- 7- 1 Oberdorf, Styria
- 7- 2 New Almaden, Calif.
- 7- 3 Traversella (2) Italy
- 7- 4 Chamouni, France
- 7- 5 Ishanimland
- 7- 6 Isle of Man, England
- 7- 7 Freiberg, Saxony
- 7- 8 Redrush, Cornwall (2)
- 7- 9 Phoenixville, Pa.
- 7-10 Mouzaia, Algeria
- 7-11 Ro Reich 23A (Styria)
- 7-12 Ro Arm 28A (Styria)
- 7-13 Ro Arm 27A (Styria)

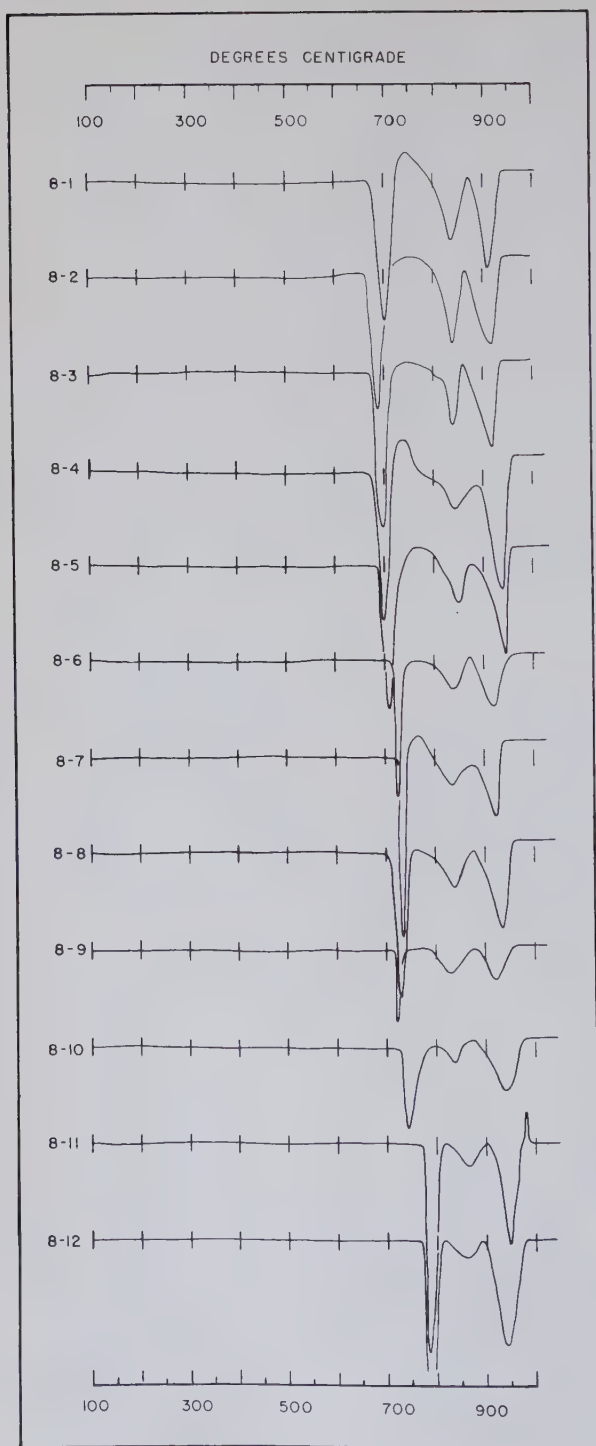


FIG. 8. DTA curves of selected ankerite specimens:

- 8- 1 Eitzterge, Styria
- 8- 2 Eisenertz, Styria
- 8- 3 Admont, Styria
- 8- 4 Gassite, Germany
- 8- 5 Ro Reich 21A (Styria)
- 8- 6 Ro Reich 24B (Styria)
- 8- 7 AEU 18A (Styria)
- 8- 8 OAM 9B (Styria)
- 8- 9 Ro Reich 22A (Styria)
- 8-10 Ro Arm 26A (Styria)
- 8-11 Brazil (1)
- 8-12 Brazil (5)

molar basis for each ion, assuming 4 moles of  $\text{CO}_2$ . These specimens were essentially free from insoluble residues but where residues were present the sample was corrected for this effect. In these computations the manganese oxide which is present in quantities up to 2%, is included in the figure for iron. Whatever assumption is made regarding Mn the conclusions are not affected.

TABLE 1

Locality	Run No.	Moles $\text{Mg}^{++}$	Moles $\text{Fe}^{++}$	Moles $\text{Fe}^{++}$ + $\text{Mg}^{++}$	Moles $\text{Ca}^{++}$
Oberdorf	7-1	1.94	0.07	2.01	2.00
Chaumoni	7-4	1.68	0.40	2.08	2.00
Freiberg	7-7	1.33	0.70	2.03	2.01
Redrush	7-8	0.93	1.05	1.98	1.95
Mouzaia	7-10	0.82	1.16	1.98	2.03
Styria 23A	7-11	0.82	1.10	1.92	1.99
Styria 28A	7-12	1.35	0.66	2.01	1.98
Styria 27A	7-13	1.02	0.88	1.90	2.04
Tri State (Beck)		1.07	0.74	1.83	2.10
Theo. dolomite		2.00	0.00	2.00	2.00
Theo. ankerite		1.00	1.00	2.00	2.00

The most striking thing about these data is the clear proof that substitution of  $\text{Fe}^{++}$  takes place exclusively in the Mg positions such that the *sum* of the moles of  $\text{Fe}^{++}$  and  $\text{Mg}^{++}$  is equal to the moles of Ca present. The consistent area under the last endothermic peak in dolomite and ankerite would be expected from these data. It will also be observed that the purest white dolomite (Oberdorf, 7-1) contains iron and that there are no apparent discontinuities in the Mg-Fe substitutions. The specimen from Redrush, Cornwall (7-8) appears to be a typical ankerite. Semi-quantitative tests show 7-4 and 7-6 to be low in iron while 7-5 and 7-9 are considerably higher.

The significance of the peaks may be interpreted with the help of x-ray powder patterns. The first peak is due to the decomposition of the magnesium positions in the lattice. This also releases the iron which becomes oxidized to  $\text{Fe}_2\text{O}_3$ .

It might be expected that the second endothermic peak is due to the formation of  $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ . This does not appear to be the case. Rather the second endothermic peak seems due to the formation of the compound  $\text{Fe}_2\text{O}_3 \cdot \text{CaCO}_3$ . A mixture of finely ground hematite and calcite in a 1:1 ratio produced the same peak as observed in these ankerite specimens. Finally after heating to 1000° C the x-ray patterns obtained from these



specimens failed to contain lines of  $\text{CaO}$  and  $\text{MgO} \cdot \text{Fe}_2\text{O}_3$  as Beck claimed for his samples, but rather strong lines of calcium ferrite  $\text{CaO} \cdot \text{Fe}_2\text{O}_3$  and  $\text{MgO}$  (diffuse). Although there is a considerable heat of reaction in the formation of  $\text{Fe}_2\text{O}_3 \cdot \text{CaCO}_3$ , it apparently does not greatly affect the heat required to liberate the carbon dioxide from the calcium ions since the last endothermic peak does not appear too greatly affected by iron content. There is some indication that the formation of this compound reduces the heat of decomposition for the residual carbonate ions.

Figure 9 shows the peak temperature of the first endothermic reaction and the area of the second endothermic peak plotted against iron con-

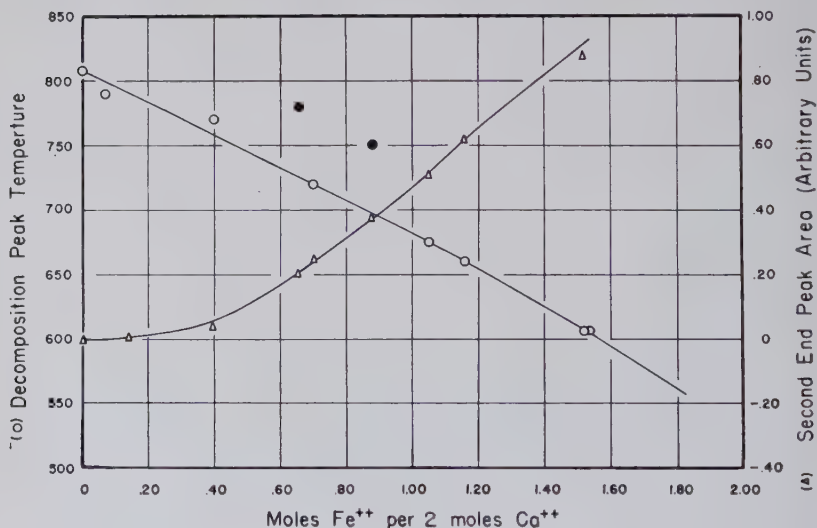


FIG. 9. Moles of substituted  $\text{Fe}^{++}$  versus decomposition peak temperature (left ordinate) and second endothermic peak area (right ordinate).

tent. The points fall on a smooth curve except for the two unusually coarse grained samples indicated as solid circles. A great difference in crystallite size will appear in a higher decomposition temperature. Once the lattice is destroyed, however, the initial grain size is not very significant hence the values of the second endothermic peak area for these same two samples fall in line. Sample 7-11, which is also quite coarse, is omitted from this figure because of the unusual overlapping of the exothermic peak on the second endothermic peak thus making it difficult to choose an accurate value for the peak area of the second endothermic reaction. It is important to observe that the second endothermic peak area against moles of  $\text{Fe}$  continues to rise after 1.00 moles of  $\text{FeO}$  has been reached. This is consistent with the formation of a 1:1 compound  $\text{Fe}_2\text{O}_3 \cdot \text{CaCO}_3$ .

If a spinel-like compound were forming between  $\text{Fe}_2\text{O}_3 \cdot \text{MgO}$  then the heat of this reaction should go through a maximum at  $\text{FeO}$  1.00 moles.

Figure 8 shows the thermal curves of a number of specimens of ankerite. The relative sensitivity between these curves and those in Fig. 7 may be compared by equating the  $\text{CaCO}_3$  decomposition peak of 7-9 and 8-1. The first five ankerites 8-1 through 8-5 are high in iron content. Thus decomposition peaks as low as  $590^\circ\text{C}$  are obtained and the second endothermic peak is correspondingly high. Sample 8-5 has a total Fe analysis of 23.1% as compared to 13.4% for 7-13. This indicates about 1.53 moles of  $\text{FeO}$ . Curves 8-6 and 8-7 show less than the first five samples but about 1.00 moles of Fe. Note the unusually homogeneous crystalline size as displayed by the extremely sharp decomposition peaks. 10–20% hematite, or other inert impurity, is indicated by the maximum peak height of the  $\text{CaCO}_3$  decomposition. 8-8 has less foreign constituent and has a wider range in crystallite size. 8-9 and 8-10 are both diluted with thermally inert constituents—mostly hematite but show a considerable difference in iron substitution in the ankerite. 8-11 and 8-12 are similar except for the exothermic peak at  $990^\circ\text{C}$  in 8-11. This was also observed on the Mouzaia sample (7-10). It is attributed to the conversion of  $\gamma\text{-Fe}_2\text{O}_3$  to hematite. Why it should be so delayed in this particular specimen is not clear. If the iron content became sufficiently high so that there was more  $\gamma\text{-Fe}_2\text{O}_3$  than that required to form  $\text{Fe}_2\text{O}_3 \cdot \text{CaCO}_3$  this might be expected. The thermal curve of 8-11 does not indicate this much iron. It is possible that this is a case of some minor iron substitution in the calcium positions. This is possible to a minor extent on theoretical grounds.

### *E. Natural Carbonate Aggregates*

Figures 10, 11 and 12 show the DTA curves for a considerable number of natural carbonate mixtures. The interpretation of these curves in terms of the foregoing discussion will illustrate the application of these concepts.

10-1 shows a sample consisting of about 80% siderite, 5–10% ankerite, and 5–10% silicate and inert. The ankerite appears to have a  $\text{Fe}:\text{Mg}$  ratio near 1:1. The chemical analysis shows:  $\text{CO}_2$  36.02%,  $\text{Fe}_2\text{O}_3$  0.46%,  $\text{FeO}$  48.09%,  $\text{MnO}$  2.67%,  $\text{CaO}$  1.59%,  $\text{MgO}$  3.19%,  $\text{SiO}_2$  6.1%. From the analysis it appears that some of the  $\text{Mg}^{++}$  is probably substituting in the siderite lattice.

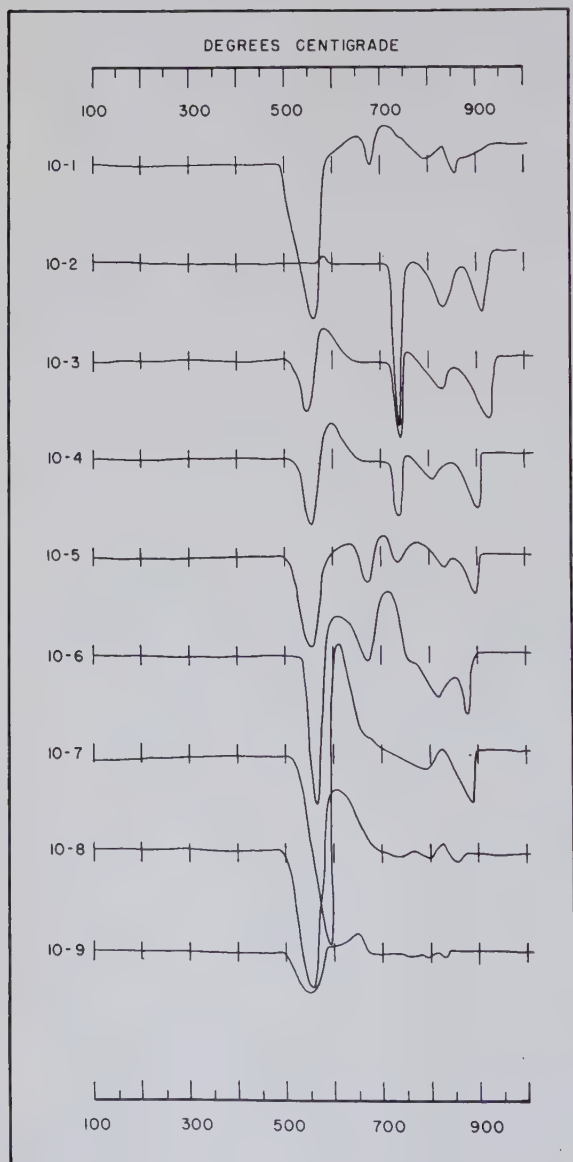


FIG. 10. DTA curves of ankerite natural aggregates from Iberg Mine, Styria, Austria:

- 10- 1 KLE 1A
- 10- 2 AEO 10B
- 10- 3 AEU 18B
- 10- 4 AEU 20A
- 10- 5 REO 6C
- 10- 6 REO 6B
- 10- 7 REO 6B-2
- 10- 8 REO 7A
- 10- 9 REU 15C



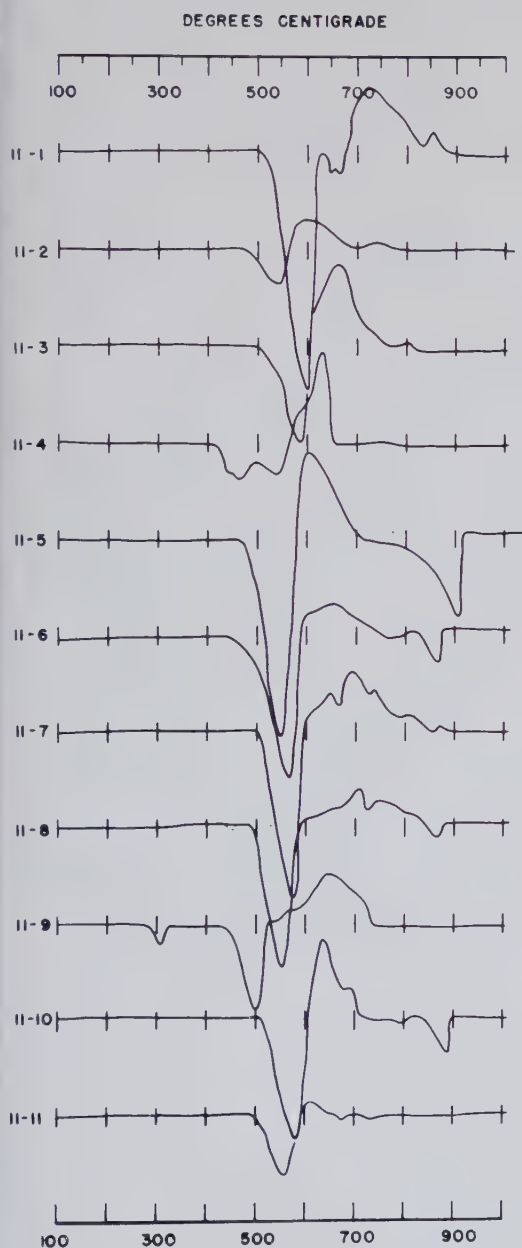


FIG. 11. DTA curves of natural siderite mixtures:

- 11- 1 Lobenstein, Germany
- 11- 2 Nassau
- 11- 3 Cornwall, England
- 11- 4 Maryland
- 11- 5 Batino, Tuscany
- 11- 6 Bear Run, Pa.
- 11- 7 REU 15A (Styria)
- 11- 8 REU 14A (Styria)
- 11- 9 Redrush (fibrous)
- 11-10 REO 7B (Styria)
- 11-11 REO 8A (Styria)

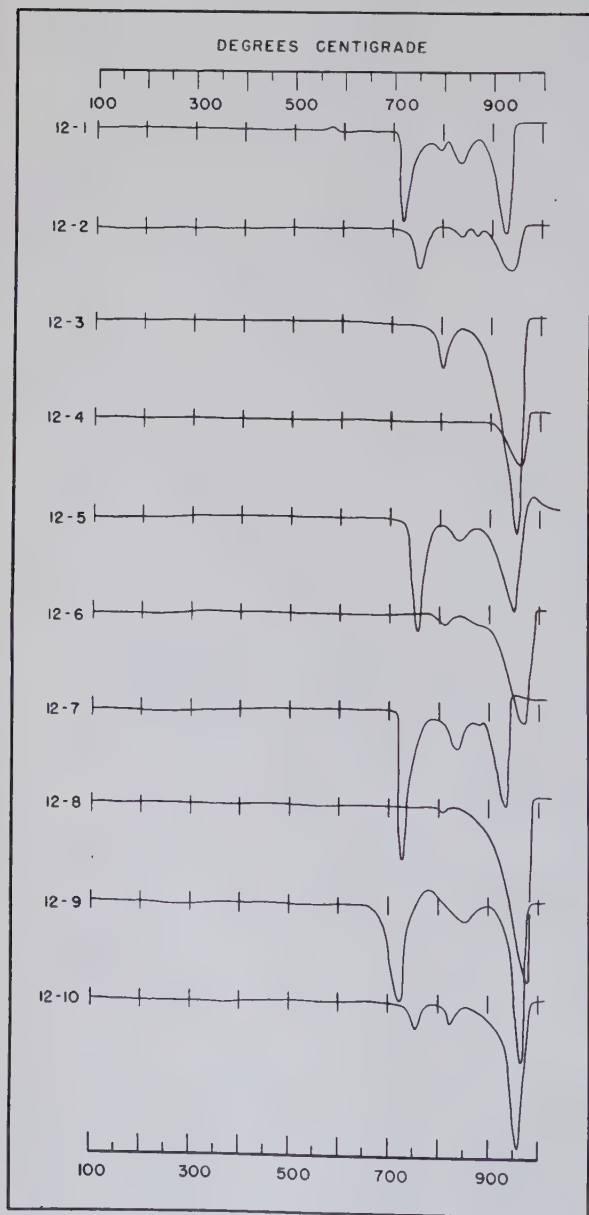


FIG. 12. DTA curves of natural carbonate aggregates:

- 12- 1 AEO 10A (Styria)
- 12- 2 AEO 12A (Styria)
- 12- 3 Ro Reich 21B (Styria)
- 12- 4 OAM 9A (Styria)
- 12- 5 AEO 11A (Styria)
- 12- 6 Ro Reich 24A (Styria)
- 12- 7 AEU 19A (Styria)
- 12- 8 REU 13A (Styria)
- 12- 9 Schemnitz, Hungary
- 12-10 Joplin, Mo.

10-2 shows the reverse of 10-1 with 3-5% siderite and 70% high iron ankerite. This sample contains 22.1% total Fe. With such a low siderite content, this indicates an ankerite with about 1.5 moles of  $\text{Fe}^{++}$ .

10-3 and 10-4 are quite similar containing about 20-30% siderite and 50-60% ankerite with about 1.00 moles of  $\text{Fe}^{++}$ . The difference in the areas of the last endothermic peak between 10-2 and 10-3 shows the effect of the greater iron content of 10-2 on the  $\text{Fe}_2\text{O}_3 \cdot \text{CaCO}_3$  decomposition.

10-5 is a most interesting specimen showing three carbonate minerals present: siderite 50%, magnesite 20% and ankerite 30% with about 1.0 moles of  $\text{Fe}^{++}$ .

10-6 appears to contain 60% siderite, 20% magnesite and 20% dolomite. 10-7 shows about 80% siderite containing some magnesium substitution with about 20% dolomite (or 10% dolomite and 10% calcite). Magnesite seems absent in this specimen although the  $\gamma\text{-Fe}_2\text{O}_3$  transformation to hematite is detectable near 680° C. 10-8 contains about 60-70% of rather pure siderite with 10% or less dolomite-ankerite. This specimen analyzed 5.32% CaO and 4.01% MgO. The x-ray pattern shows only siderite lines. 10-9 shows about 20% siderite and 5% ankerite. The major impurity in 10-9 is hematite. The specimen analyzed 38.5% total Fe.

11-1 appears to be a high grade siderite except for the little doublet between 600 and 700° C. This appears to be due to two differently substituted magnesites. 11-2 simply contains 20% siderite with inert material. 11-3 may contain two siderites which add up to about 40%. 11-4 contains sulfides and siderite. The dominance of the exothermic peak over the endothermic peak is due to the rapidity of oxidation. The size of the exothermic peak indicates the presence of 30-50% siderite. The peaks between 400 and 500° C are attributed to the sulfides. 11-5 consists of 80% siderite and 20% fine calcite. 11-6 has 60% siderite and 10% calcite. There is the possibility of a few per cent of dolomite. 11-7 contains 75% siderite with some Ca substitution, 5% magnesite and a few per cent of dolomite. This specimen analyzed 6.93% CaO, 3.14% MgO, and 19.7% insoluble. 11-8 contains 50-60% siderite, 5% calcite and a trace of dolomite. This specimen has a total iron content of 35.20% Fe indicating hematite as an impurity. 11-9 shows 5% goethite (300° C), 40% of a very fine siderite and no other carbonates. 11-10 shows 70% siderite with considerable Mg substitution, 10% calcite and a few per cent dolomite. 11-11 shows an impure siderite (est. 20%). It is mixed with considerable hematite. The total analysis for 11-11 is 41.2% Fe.

12-1 appears to contain 2-3% siderite, 70% ankerite and about 0.8 moles of Fe and 10% dolomite. This specimen analyzed 9.56% MgO



and 23.10% CaO. The FeO was 20.2%. 12-2 is similar to 12-1 but contains no trace of siderite and has nearer to 30% ankerite. The total Fe content of 26.6% indicates some hematite which was observed in the x-ray patterns. 12-3 is a dolomite (20%), calcite (80%) mixture. The total iron content of this specimen was 2.75% which was present largely as a hematite stain. 12-4 is an ironstained calcite (20%). 12-5 is a reasonably low iron ankerite with relatively minor inert impurities (10–20%). The substituted iron is estimated at 0.6 moles of Fe from the thermal diagram. The total iron analysis of 8.25% is consistent with this interpretation. 12-6 suggests 10% dolomite, 50% calcite and inerts. 12-7 is a reasonably pure ankerite containing about 1.00 moles of Fe. The total iron analysis was 13.9%. The slight peak at 880° C indicates some admixed dolomite.

12-8 is a rather pure calcite with 5% dolomite present. 12-9 appears to be an ankerite with about 0.5 moles of Fe. 10–20% of excess calcite seems present. The chemical analysis clearly indicates calcite mixing: CaO 38.28%, MgO 9.30%, FeO 9.29%, and CO<sub>2</sub> 44.20%. 12-10 shows 10–20% high iron ankerite with 50% calcite.

## V. DISCUSSION

This study has thrown some light on the extent of substitution found among the common carbonate minerals. Figure 13 furnishes a trilinear plot of the data on samples whose mineral composition has been determined either in this study or elsewhere. The discontinuity between the calcite type of lattice (calcite, magnesite, and siderite) and the ankerite lattice is very striking. Apparently there is sufficient energy difference between randomly substituted Mg-Fe ions in the calcite lattice and an ordered (layered) structure, that in nature one or the other forms. Many of the specimens studied in this work were mixtures of lattices. This emphasizes the energy differential between the two structures. It is also clear that in the ankerite lattice Fe substitutes for Mg without any break but that there is negligible substitution of Mg or Fe in the Ca positions. Thus all of the ankerite specimens on which chemical data exist in this study fall on the horizontal line of 50% Ca. Complete substitution is observed between Fe<sup>++</sup> and Mg<sup>++</sup> but in the direction of Ca the substitution is restricted to about 10%. Likewise the few analyzed calcite specimens show little substitution. It is possible that some of the separation is due to the geochemical conditions of formation. However, the intimate intergrowth of siderite and calcite or siderite and ankerite suggests the main reason for the lack of more substitution is lattice potential energy differences.

In the study on rhodochrosite (Kulp, Wright, and Holmes, 1949),

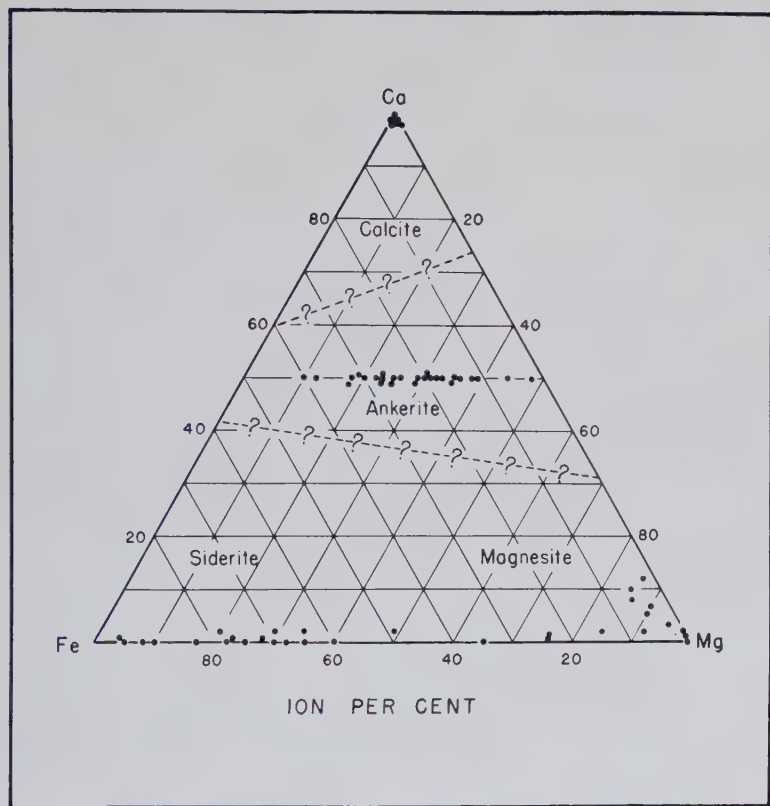


FIG. 13. Composition-phase diagram for Ca-Fe-Mg carbonates. Most of the specimens are taken from this study.

sufficient specimens were obtained to indicate the complete ionic substitution of  $\text{Mn}^{++}$  to  $\text{Ca}^{++}$  in nature. Minerals have also been reported which clearly indicate a similar series between  $\text{Fe}^{++}$  and  $\text{Mn}^{++}$ . The data are meagre with regard to the Mg-Mn series. This is probably due to the rarity of the individual minerals and the special geochemical conditions requisite to the formation of both being present at the same time. These relationships appear reasonable on the basis of the ionic radii of  $\text{Ca}^{++}$  1.06:  $\text{Mn}^{++}$  0.91:  $\text{Fe}^{++}$  0.83: and  $\text{Mg}^{++}$  0.78 Å.

The results presented above indicate the usefulness of thermal analysis in elucidating the mineral composition of natural carbonate aggregates. The peaks are so sensitive to substitution that it is possible to estimate the cation composition of each phase. The peaks are sufficiently large so that the method could be used to great advantage in the study of car-

bonate mineralization in the field. A portable DTA apparatus such as described by Hendricks et al. (1946) should be quite satisfactory for many types of field studies. Where rapid chemical and mineralogical data on carbonates are required, the thermal method offers many advantages.

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# STUDIES OF URANIUM MINERALS (VIII): SABUGALITE, AN ALUMINUM-AUTUNITE\*

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## ABSTRACT

Sabugalite is a new member of the autunite group with the composition  $\text{HAL}(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$ . Analyses are cited of material from the Mina da Quarta Seira, Sabugal, Beira province, and from Kariz, Minho province, in Portugal; a third occurrence is noted from Bendada in Beira province. Sabugalite is a secondary mineral found associated with meta-autunite, saléeite and phosphuranylite. It occurs as crusts of yellow platy crystals with perfect cleavage {001}. Hardness  $2\frac{1}{2}$ ; gravity 3.20. Air dried sabugalite optically has an anomalous biaxial negative character with  $n_X = 1.564\text{--}1.565$  (colorless),  $n_Y = 1.581\text{--}1.583$  (yellow),  $n_Z = 1.582\text{--}1.584$  (yellow), and  $2V = 0^\circ$  to moderate. X-ray study indicates a tetragonal cell with  $a_0 = 6.96 \text{ \AA}$ ,  $c_0 = 19.3$ ;  $a_0:c_0 = 1:2.773$ ; cell contents  $\text{HAL}(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$ . Sabugalite is isostructural with fully-hydrated autunite,  $\text{Ca}_2(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$ , with  $\text{Al}'''+\text{H}' = 2\text{Ca}''$ . Sabugalite breaks down between  $68^\circ$  and  $101^\circ$  to a new phase isostructural with the artificial meta-II hydrate of autunite and does not form an intermediate meta-I hydrate with halved cell contents as does fully-hydrated autunite. The water content of the fully-hydrated and meta-II hydrates of sabugalite varies zeolitically with accompanying variation in the indices of refraction.

The new uranium mineral here described under the name sabugalite has the composition  $\text{HAL}(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$  and is isostructural with fully-hydrated autunite,  $\text{Ca}_2(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$ . The mineral has been recognized on specimens from three different localities in a suite of uranium minerals from Portugal acquired in 1932 with the collection of the Portuguese mineralogist A. d'O. Bello. Sabugalite very closely resembles autunite and like that species is of secondary origin. A specimen from the Mina da Quarta Seira, Sabugal, Beira province, shows a thick crust of sabugalite on a brecciated mass of milky quartz and feldspar. Other specimens from this place contain meta-autunite, saléeite and phosphuranylite as crusts upon deeply altered granitic or pegmatitic rock. Material from Kariz in Minho province shows brecciated milky quartz and kaolinized feldspar apparently of pegmatitic origin that is thickly coated with sabugalite admixed with and underlain by meta-autunite. A specimen from Bendada, Beira province, shows a thin coating of sabugalite intergrown with meta-autunite and perhaps also saléeite on a slab of quartzose and limonitic vein material.

Sabugalite has a bright yellow to lemon yellow color. It typically occurs as densely aggregated crusts of very thin platy crystals up to about one millimeter on edge. The mineral is probably tetragonal in crystallization. Individual plates are square or lath-like in shape and are bounded laterally by very narrow and indistinct faces of {100} and {h0l}. A few

\* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 330.

relatively perfect crystals under the microscope were observed to have their corners truncated at  $45^\circ$  by tiny faces of  $\{hkl\}$ . The plane of flattening,  $\{001\}$ , is uneven or warped and subparallel growths joined on this surface are very common. Morphological measurements could not be obtained. The plates are somewhat flexible and have a perfect cleavage parallel to  $\{001\}$ . The hardness is  $2\frac{1}{2}$  and the specific gravity, measured by suspension in heavy liquids, is approximately 3.20.

*Optical Properties and Fluorescence.* Samples of sabugalite air dried at room temperature are biaxial negative with 2V somewhat variable but usually moderately large. Some flakes were noted, especially in the material from Kariz, to be sensibly uniaxial or to have an optic angle of only a few degrees. The departure from uniaxiality in this probably tetragonal species is believed due, as in other members of the autunite group,<sup>1</sup> to variation in the content of zeolitic water within the limits of stability of the phase. The plates ordinarily extinguish uniformly. A few plates showed a mottled extinction but none were observed to exhibit the sectoral structure with varying optical orientation therein such as has been described<sup>1</sup> in other members of the autunite group. The X (or E) vibration direction is perpendicular to the flattening. It is curious to find in lath-like  $\{001\}$  plates that Z always is parallel to the elongation. This is true not only of sabugalite but also of zeunerite, saléeite and autunite. The optical data for natural sabugalite are listed in Table 1. Optical data on artificial dehydration products of sabugalite are cited beyond in Table 6.

TABLE 1. OPTICAL DATA FOR AIR DRIED SABUGALITE

	Mina da Quarta Seira	Kariz	Bendada	Pleochroism
$n_X$ or $n_E$	1.564	1.564	1.565	Colorless
$n_Y$	1.582	1.581–1.583	1.581–1.582	Pale yellow
$n_Z$ or $n_O$	1.584	1.583	1.582	Pale yellow
2V	moderate	small to moderate	$0^\circ$ to moderate	

Air dried sabugalite fluoresces a bright lemon yellow in both long-wave and short-wave ultraviolet radiation although somewhat more intensely in the long wave-lengths. Slightly dehydrated material obtained by heating fresh sabugalite to temperatures of  $44^\circ$  or  $68^\circ$  also fluoresces lemon-yellow but somewhat less intensely, and the meta-II hydrate obtained

<sup>1</sup> Beintema, J., *Rec. Trav. Chim. Pays-Gas*, **57**, 155 (1938); Hallimond, A. F., *Minerol. Mag.*, **17**, 326 (1916); **19**, 43 (1920); Rinne, J. F., *Cbl. Min.*, 618, 709 (1901).

by heating to  $135^\circ$  is very weakly fluorescent; in both cases the fluorescence is slightly stronger in long-wave than in short-wave radiation. This variation in intensity of fluorescence with water content also is shown by the analogous hydrates of zeunerite<sup>2</sup> and autunite.

*X-Ray Crystallography.* X-ray powder photographs of sabugalite are very similar to those of fully-hydrated saléeite,  $\text{Mg}_2(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$ , and resemble but are distinct from those of both fully-hydrated autunite and meta-autunite. The photographs yielded by the substance unfortunately are of poor quality. X-ray rotation and Weissenberg films taken on cleavage flakes also were rather unsatisfactory. Usable photographs could not be obtained about [001] due to the very thin and warped nature of the crystals. Rotation photographs taken about the horizontal axes showed much continuous streaking along the layer-lines, together with crystal disorientation effects due to subparallel growth, and these features were repeated on the Weissenberg resolutions. The single-crystal photographs were indexed in terms of a tetragonal cell with  $a_0 = 6.96 \text{ \AA}$  and  $c_0 = 19.3$ . The powder photograph also can be indexed in terms of this cell (Table 2), but with some uncertainty due partly to diffuseness of the lines. The principal difficulty is in the interpretation of the faint line with  $d = 5.59$ . This line approximates to (102) in the cell stated, but then is the only reflection present with  $h+k+l$  odd and is contrary to the extinction requirements in the space group of fully-hydrated autunite,

TABLE 2. X-RAY POWDER SPACING DATA FOR SABUGALITE

*Indexing for cell with  $a_0 = 6.96 \text{ \AA}$ ,  $c_0 = 19.3$ , obtained from single-crystal measurements, Cu/Ni*

<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (meas.)	<i>I</i>	<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (meas.)	<i>I</i>
002	9.650	9.69	10	220	2.461	2.452	2
101	6.548	6.56	1	222	2.384	2.389	2
102	5.644	5.59	1	303	2.183	2.188	6
004	4.825	4.86	9	310	2.201		
112	4.384	4.39	4	323	1.792	1.792	1
200	3.480	3.47	8	400	1.740	1.726	1
114	3.345	3.36	1	330	1.640	1.641	$\frac{1}{2}$
006	3.216	3.22	$\frac{1}{2}$	404	1.637		
211	3.072	3.06	$\frac{1}{2}$	420	1.556	1.552	1
204	2.822	2.818	1	510	1.364	1.364	1

$I4/mmm$ , with which substance sabugalite is presumed to be isostruc-

<sup>2</sup> Frondel, J. W., *Am. Mineral.*, **36**, 249-255 (1951).



trual. It also may prove that sabugalite is actually orthorhombic and only pseudo-tetragonal. The pattern can not be completely indexed in terms of a cell with  $a_0 = 6.96 \text{ \AA}$  and  $c_0$  halved to 9.65. This point is of some importance since the  $19.3 \text{ \AA}$  period is characteristic of the fully-hydrated phases in the autunite group, while the meta-I hydrates have a cell with an identical  $a_0$  but with  $c_0$  halved. The x-ray data indicates that sabugalite has the structure of the fully-hydrated phase. A comparison of the unit cell dimensions of sabugalite and some other members of the autunite group is given in Table 3.

TABLE 3. UNIT CELL DIMENSIONS OF SOME MINERALS  
OF THE AUTUNITE GROUP

	Sabugalite	Saléeite <sup>a</sup>	Autunite <sup>b</sup>
Space group		$I4/mmm$	$I4/mmm$
Cell contents	$\text{HAl}(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$	$\text{Mg}_2(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$	$\text{Ca}_2(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$
$a_0$	$6.96 \text{ \AA}$	7.01	7.00
$c_0$	19.3	19.84	20.67
$a_0:c_0$	1:2.773	1:2.830	1:2.952

(a) By powder method on analyzed material from Mina da Quarta Seira, Sabugal, Portugal.

(b) Beintema (1937).

*Chemistry.* Complete chemical analyses were made of the sabugalite from the Mina da Quarta Seira in Beira province and from Kariz in Minho province. These are cited in Table 4. The material from Mina da Quarta Seira was treated in heavy liquids, which removed traces of quartz and meta-autunite, and the analysis sample was entirely homogeneous under the microscope. Meta-autunite is quite easily distinguished because of its higher indices of refraction. The material from Kariz was rather intimately intergrown with meta-autunite and this proved very difficult to remove from the sample because its gravity in part overlapped that of the sabugalite. The first sample of this material prepared by treatment in heavy liquids afforded on partial analysis  $\text{CaO}$  0.84,  $\text{P}_2\text{O}_5$  13.91,  $\text{As}_2\text{O}_5$  2.71. A second sample, ground more finely and fractionated closely in the heavy liquids, gave the analytical results cited in Table 4. This sample was estimated optically to contain about 5 per cent of meta-autunite, and the amount of  $\text{CaO}$  found in the analysis roughly corresponds to this figure. The Ca hence has been disregarded in the calculation of the formula. The material from Bendada in Beira

TABLE 4. ANALYSES OF SABUGALITE  
Analysis 1: Mina da Quarta Seira, Beira.

Weight per cent		Molecular quotient	Atomic quotient	Experimental cell contents ( $\times 1802/100$ )	Theoretical cell contents	Theoretical weight per cent
Al <sub>2</sub> O <sub>3</sub>	2.65	.0260	Al .052	0.94	1	Al <sub>2</sub> O <sub>3</sub> 2.87
UO <sub>3</sub>	65.22	.2280	U .228	4.11	4	UO <sub>3</sub> 64.41
P <sub>2</sub> O <sub>5</sub>	16.08	.1133	P .226	4.08	4	P <sub>2</sub> O <sub>5</sub> 15.99
H <sub>2</sub> O	15.93	.8842	H 1.768	31.9	33	H <sub>2</sub> O 16.73
Total	99.88		O 2.213	39.9	40	Total 100.00

Analysis 2: Kariz, Minho.

CaO	0.36					
Al <sub>2</sub> O <sub>3</sub>	3.20	.0314	Al .063	1.13	1	
UO <sub>3</sub>	65.01	.2273	U .227	4.08	4	
P <sub>2</sub> O <sub>5</sub>	14.02	.0987	P .197	3.55	3.97	4
As <sub>2</sub> O <sub>5</sub>	2.70	.0117	As .023	0.42		
H <sub>2</sub> O	[14.71]					
Total	[100.00]					

1. Sabugalite. Mina da Quarta Seira, Sabugal, Beira province, Portugal. Analysis by F. A. Gonyer, 1950. Following elements sought and found absent: Ca, Mg, Ba, Cu, Fe, Mn, As. The theoretical weight per cent cited corresponds to the formula  $\text{HAl}(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$ .
2. Sabugalite. Kariz, Minho province, Portugal. Analysis by F. A. Gonyer, 1950. With MgO trace. CaO due to admixed meta-autunite. A direct water determination on material probably containing a slightly larger amount of meta-autunite gave 16.78 per cent.

province was a mixture of at least three components of about the same specific gravity, including meta-autunite and apparently also saléeite, and a reasonably pure analysis sample could not be obtained. Chemical tests of this material proved the presence of Ca, Mg and Al in addition to U and P.

The unit cell contents of the two analyzed samples, calculated directly from the measured molecular weight of the cell, 1802, indicates that the formula of the mineral is



A small amount of As substitutes for P in the material from Kariz, with As:P=1.17:10. The average of the two analyses is somewhat closer to

the formula than either analysis alone. The agreement in any case is satisfactory, especially in view of the isostructural relation to autunite,  $\text{Ca}_2(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$ , indicated by the x-ray work. This relation may be discussed in some detail in view of the interesting composition of the substance and of the question of the existence of a meta-I hydrate of sabugalite analogous to meta-autunite.

As shown by Beintema,<sup>1</sup> the crystal structure of autunite consists of  $(\text{PO}_4)$  tetrahedra and deformed  $(\text{UO}_6)$  octahedra that are linked by the sharing of corners into two-dimensional sheets on  $\{001\}$ . The U-O coordination group is deformed in such way that two oxygen atoms are more closely associated with the  $\text{U}^6$  ion, giving rise to the so-called uranyl ion  $(\text{UO}_2)^2$ . The water molecules and the Ca ions (or Mg, Ba, Cu,  $\text{Fe}^{++}$  in other members of the group) occupy relatively large cavities between the layers. The unit cell contents are  $\text{Ca}_2(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{--}20\text{H}_2\text{O}$ . The Ca ions occupy the two-fold positions in  $(a)$  of  $I4/mmm$ . When the water content is reduced below about  $16\text{H}_2\text{O}$  by heating or desiccation, the structure breaks down to that of a new phase, meta-autunite-I. On further dehydration, the meta-I phase breaks down into a still lower hydrate, meta-autunite-II, the structure of which is unknown. The principal difference between the structure of the meta-I phase and that of fully-hydrated autunite is in the way in which the  $(\text{UO}_6)(\text{PO}_4)$  layers are stacked. During the transformation to the meta-I phase, the individually unchanged layers are moved over a distance  $[\frac{1}{2}\frac{1}{2}0]$  with respect to each other. The geometry of this change maintains the  $a$ -axis period, but halves the  $c$ -axis period, the initial body-centered cell transforming into two primitive cells of the meta-I phase. The symmetry remains tetragonal. The new cell contents are then  $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The new space-group  $P4/nmm$ , however, affords only a two-fold position for the single Ca ion and this ion is believed to be distributed statistically over half of the available positions. The ready base-exchange of the inter-layer cations and the zeolitic dehydration phenomena within the limits of stability of the phase are both consequences of the relatively open layer-type structure. In the meta-I phase, the Ca can be replaced by direct crystallization or by base-exchange by twice the number of monovalent ions such as Na, K,  $\text{NH}_4$  or H. The monovalent cations then wholly occupy the two-fold positions. The latter ions can not be obtained in crystals of the fully-hydrated structure-type, however, because space is lacking for a sufficient number to be introduced to effect valence compensation with the  $(\text{UO}_6)(\text{PO}_4)$  layers. Treatment of fully-hydrated autunite in strong solutions of base-exchangeable monovalent cations results in a conversion to the meta-I hydrate.

In the present instance, sabugalite appears to belong to the fully-

hydrated phase rather than the meta-I phase. The calculated unit cell contents conform to the autunite-type but with one trivalent Al ion in place of the two divalent Ca ions of autunite. It is presumed that the Al ion is distributed statistically over the two-fold position taken by the Ca in autunite, and that valence compensation is effected by the concomitant presence of one H' ion, with  $Al''' + H' = 2Ca''$ . If this interpretation is correct, it appears that sabugalite should not form a meta-I hydrate isostructural with meta-autunite since the halving of the cell volume thus brought about would admit only halved  $Al'''$  and H' ions. Dehydration data for sabugalite described beyond indicate that this substance does not form a meta-I hydrate but breaks down directly from the fully hydrated phase to the meta-II phase.

*Dehydration Data.* Samples of fresh, air-dried sabugalite were heated to essentially constant weight at temperatures of 44°, 68°, 101°, 117°, 135° and 165° C. No change in the x-ray powder pattern was found in the samples heated at 44° and 68°, although there was a small loss of water and an increase in the indices of refraction. The samples heated at 135° and 165°, however, afforded an entirely new pattern which proved on direct comparison to be virtually identical with that of the meta-II hydrate of autunite. The spacing data for this pattern are listed in Table 5. The samples heated at 101° and 117° proved to represent mixtures of

TABLE 5. X-RAY POWDER SPACING DATA FOR THE META-II HYDRATE OF SABUGALITE.

Cu/Ni (in Å). Heated at 135°.

<i>d</i> (meas.)	<i>I</i>	<i>d</i> (meas.)	<i>I</i>
8.51	10	2.21	1
5.5-4.3	diffuse region	2.17	1
3.51	7	2.02	2
3.23	5	1.91	1
2.99	6	1.87	1
2.84	2	1.74	1

the meta-II phase and still undecomposed remnants of the fully-hydrated phase. The temperature of breakdown of the fully-hydrated to the meta-II phases thus is between 68° and 101°. The pattern of the fully hydrated phase after heating at 44° and 68° was identical with that of the unheated material. The pattern afforded by the still undecomposed remnants of this phase in samples heated at 101° and 117° showed a marked diffuseness of the line at  $d=4.86$ , although the few other lines remaining of the pattern were relatively sharp, and there was a progressive decrease in the spacing of the innermost, most intense line of the



pattern. At room temperature,  $44^\circ$  and  $68^\circ$  this line of the fully-hydrated phase had  $d$  essentially constant at 9.70; at  $101^\circ$   $d=9.12$ ,  $117^\circ$   $d=8.63$ ,  $135^\circ$   $d=8.51$ ,  $165^\circ$   $d=8.16$ . No pairing of lines was observed in this region that could be attributed to admixture, and the (002) reflection of the sabugalite apparently passes continuously into the meta-II pattern. The two phases may be structurally related, with their (001) layers parallel, and the spacings of (011) in the meta-II phase vary with the content of zeolitic water (?) held between the layers.

Data on the water content and optical properties of the heated samples are summarized in Table 6. Optically, none of the samples were

TABLE 6. DEHYDRATION DATA FOR SABUGALITE (MINA DA QUARTA SEIRA)

Sample	Phase	Optical Properties				Per cent loss of original H <sub>2</sub> O
		$n_X$	$n_Y$	$n_Z$	2V	
Unheated. Airdried.	Fully-hydrated	1.564	1.582	1.584	mod.	0
Heated at $44^\circ$	Fully-heated		1.591	1.594	mod.	3.4
Heated at $68^\circ$	Fully-hydrated	1.575	1.596	1.597	small	20
Heated at $101^\circ$	Mixture					57
Heated at $117^\circ$	Mixture					63
Heated at $135^\circ$	Meta-II	1.592	1.604	1.618	large	82
		to	to	to		
Heated at $165^\circ$	Meta-II	1.596	1.608	1.623	large	91
Cooled from $135^\circ$ and held over water.	Meta-II	Part:	1.577	< 1.59	large	
			to	to		
		Mostly:	1.581	1.587	large	
			to	to		
		Part:	> 1.59	~ 1.602	large	

entirely homogeneous, including those which gave  $x$ -ray patterns indicating the presence of one phase only. The variation is believed to be due to minor differences in zeolitic water content between different grains in material that had not been heated sufficiently long to reach equilibrium. The optical data given represent the values afforded by the great bulk of the sample in each case. The indices of the fully-hydrated phase are seen to increase with decreasing content of zeolitic water within the limit of stability of the phase. When samples of this phase heated at  $44^\circ$  and  $68^\circ$  are held in a moist atmosphere at room temperature the indices decrease to practically the original values with no accompanying change in the  $x$ -ray pattern. Unheated sabugalite when placed in water at room temperature decreases very slightly in indices and the  $x$ -ray

pattern does not change. Heated samples of the meta-II phase when placed in a moist atmosphere at room temperature decrease markedly in indices (Table 6) but the *x*-ray pattern remains that of the meta-II phase. The breakdown between the fully-hydrated and meta-II phases thus is not reversible. The samples heated at 135° and 165° showed a considerable variation in indices, with most of the grains in the range cited.

The dehydration phenomena of sabugalite are similar to those of autunite except that a meta-I hydrate is not found in sabugalite. Fully-hydrated autunite breaks down into the meta-I hydrate near room temperature, depending on the humidity, and the change is reversible. The meta-I hydrate in turn breaks down irreversibly into the meta-II hydrate at about 80°. Fully-hydrated zeunerite behaves similarly.<sup>2</sup> The indices of refraction of the fully-hydrated, meta-I and meta-II phases of autunite and zeunerite all vary with the content of zeolitic water within the stability range of the phase itself. The fact that samples of sabugalite do not change in *x*-ray pattern when immersed in water at room temperature indicates that the phase represented is already the fully-hydrated one as indicated by the unit cell dimensions. The observation is not critical, however, because different samples of the meta-I phase of both torbernite and zeunerite rehydrate to the fully-hydrated phase with markedly different ease and some samples apparently do not reconvert at all.

The dehydration data of Beintema<sup>1</sup> indicates that the fully hydrated phase of autunite,  $\text{Ca}_2(\text{UO}_2)_4(\text{PO}_4)_4 \cdot n\text{H}_2\text{O}$ , is stable with  $n > 10\frac{1}{2}\text{H}_2\text{O}$ , the meta-I phase with  $n$  from  $2\frac{1}{2}$  to  $6\frac{1}{2}\text{H}_2\text{O}$  and the meta-II phase with  $n$  from 0 to about  $6\text{H}_2\text{O}$ . The data for sabugalite are comparable.

*Synthesis.* Efforts to synthesize sabugalite have been unsuccessful. In one set of experiments, solutions of uranyl nitrate and aluminum chloride in molar ratios up to  $\text{U}:\text{Al}=1:2.5$  were precipitated by the calculated amount of  $\text{H}_3\text{PO}_4$ . These gave products identical with hydrogen-autunite,  $\text{H}_2(\text{UO})_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ . It may be noted that hydrogen-autunite also precipitates in place of autunite from solutions containing Ca when the acidity is high. Efforts to obtain sabugalite by reaction of a saturated solution of aluminum acetate in acetic acid with uranyl acetate and ammonium hydrogen phosphate gave negative results, as did an effort to base-exchange washed hydrogen-autunite with a 1N water solution of aluminum chloride.

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# STUDIES OF URANIUM MINERALS (IX): SALÉEITE AND NOVACEKITE\*

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## ABSTRACT

Novacekite, a new uranium mineral from Schneeberg, Saxony, has the composition  $\text{Mg}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$  and forms a probably complete series to the phosphate analogue, saléeite. Analyzed material with  $\text{As}:\text{P} \sim 1:1$  is tetragonal with  $a_0 = 7.12 \text{ \AA}$ ,  $c_0 = 20.14$  and gravity 3.3. Optically this material, like the other members of the series, has an anomalous biaxial negative character, with  $n_Y = n_Z = 1.620\text{--}1.623$  and  $2V \ 0^\circ$  to  $15^\circ$ . The unanalyzed but essentially pure end-component, also from Schneeberg, has  $a_0 = 7.16 \text{ \AA}$ ,  $c_0 = 20.19$ ; biaxial negative with  $n_X = 1.620$ ,  $n_Y = n_Z = 1.637$ ,  $2V \ 0^\circ$  to  $15^\circ$ ; gravity 3.6. An analysis is given of a new occurrence of saléeite,  $\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ , at Mina da Quarta Seira, Sabugal, Portugal; tetragonal with  $a_0 = 7.01 \text{ \AA}$ ,  $c_0 = 19.84$ ; biaxial negative with  $n_X = 1.565$ ,  $n_Y = 1.582$ ,  $n_Z = 1.585$ ,  $2V \sim 65^\circ$ ,  $r > v$ . Saléeite from Shinkolobwe, Belgian Congo, has  $a_0 = 7.02 \text{ \AA}$ ,  $c_0 = 19.81$ ;  $n_X = 1.554$ ,  $n_Y = n_Z = 1.571$ ,  $2V \ 0^\circ$  to  $10^\circ$ . Novacekite and saléeite closely resemble and are isostructural with fully-hydrated autunite. The indices of refraction vary with the content of zeolitic water within the limits of stability of the fully-hydrated phase.

## SALÉEITE FROM PORTUGAL

A description of the rare uranium mineral saléeite has been given in a preceding paper of this series.<sup>1</sup> A new occurrence of this mineral has been identified in a suite of secondary uranium minerals from Portugal. The locality is the Mina da Quarta Seira, Sabugal, Beira Province, Portugal. The mineral occurs as tiny, thin rectangular plates that are interleaved into a coherent but very porous aggregate. Many crystals are subparallel growths on  $\{001\}$  and none are measurable. The color is pale canary-yellow to straw-yellow. Other specimens from the same locality show deeply weathered pieces of granite or fine-grained pegmatite thickly incrustated with meta-autunite, sabugalite and minor amounts of phosphuranylite.

A chemical analysis of the mineral, cited in Column 3 of Table 2, shows that it conforms to the formula  $\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 9\text{H}_2\text{O}$ . A small amount of Pb and apparently also Al substitutes for Mg. The x-ray powder diffraction photograph indicates that this material, like the arsenatian saléeite with approximately  $10\text{H}_2\text{O}$  from Schneeberg described by Mrose,<sup>1</sup> is isostructural with fully-hydrated synthetic autunite as prepared by the method of Beintema.<sup>2</sup> The water content (approximately  $8\text{H}_2\text{O}$ ) and the optical properties of the original saléeite<sup>3</sup> from Shinkolo-

\* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 331.

<sup>1</sup> Mrose, M. E., *Am. Mineral.*, **35**, 525–530 (1950).

<sup>2</sup> Beintema, J., *Rec. Trav. Chim. Pays-Bas*, **57**, 155 (1938).

<sup>3</sup> Thoreau, J., and Vaes, J. F., *Bull. soc. belge géol.*, **42**, 96 (1932).

bwe, Belgian Congo, suggests that this particular material corresponds to the meta-I hydrate of autunite. Two specimens of saléeite from Shinkolobwe, one originally from the collection of A. Schoep and obtained through the U. S. National Museum, and the other loaned through the courtesy of Professor P. F. Kerr of Columbia University, were checked in this regard and both were found to have the structure of the fully-hydrated phase. The Shinkolobwe and Portuguese material has practically identical tetragonal cell dimensions (see Table 1).

Under the microscope, the saléeite from Portugal appears as rectangular plates with the corners sometimes truncated at 45°. The mineral is

TABLE 1. OPTICAL PROPERTIES AND UNIT CELL DIMENSIONS  
IN THE SALÉEITE-NOVACEKITE SERIES

Name	Saléeite	Saléeite	Saléeite	Arsenatian saléeite	Phosphatian novacekite	Novacekite
Locality	Shinkolobwe <sup>a</sup>	Shinkolobwe <sup>b</sup>	Portugal	Schneeberg <sup>c</sup>	Schneeberg	Schneeberg
Anal. No.	2	(Qual. only)	3	4	5	(Qual. only)
P:As ratio	No As	No As	No As	1:0.22	1:1.01	Trace of P
$n_X$ or $n_E$	1.559	1.554	1.565	1.559		1.620
$n_Y$	1.570	1.571	1.582	1.574	1.620-1.623	1.637
$n_Z$ or $n_O$	1.574	1.571	1.585	1.574	1.620-1.623	1.637
2V	61°	0°-10°	65°	0°	0°-15°	0°-15°
Disp.	$r > v$		$r > v$		$r > v$	$r > v$
$a_0$		7.02 Å	7.01	7.05	7.12	7.16
$c_0$		19.81	19.84	19.87	20.14	20.19
$a_0:c_0$		2.823	2.830	2.819	2.829	2.820

All members of the series are pleochroic with X (or O) = nearly colorless, Y = pale yellow, Z = (or E) pale yellow.

<sup>a</sup> Thoreau and Vaes (1932).

<sup>b</sup> New data on specimen from U. S. National Museum.

<sup>c</sup> Mrose (1950). Original single-crystal measurements reported as  $a_0 = 6.98$ ,  $c_0 = 19.813$ ; present data from powder film of original sample.

biaxial negative, with 2V about 65° and with X perpendicular to the flattening. The plates extinguish uniformly and do not have a mosaic structure of varying optical orientation such as is shown by the original Shinkolobwe material. The optical properties of air dried saléeite from its known occurrences are given in Table 2, beyond, together with those of the isostructural arsenate, novacekite, described in the following section. The unheated saléeite from Portugal when kept in moist air at room temperature for 30 days decreased slightly in indices of refraction, with  $n_Y = 1.578$  and  $n_Z = 1.581$ . A sample when heated in air at 92° C for 48 hours was found to have lost water with an accompanying increase in indices to  $n_X = 1.592$ ,  $n_Y = 1.603$ ,  $n_Z = 1.614$  and 2V large. After



standing at room temperature in a moist atmosphere for 40 days the indices returned almost to the original values.

#### NOVACEKITE, AND THE SALÉEITE—NOVACEKITE SERIES

In the course of examination of a small suite of secondary uranium minerals from Schneeberg, Saxony, that were suspected to consist of uranospinite or troegerite, two specimens were found of a mineral that has proved to be a new hydrated magnesium uranyl arsenate member of the autunite group. The name novacekite is proposed for this species after the Czech mineralogist Radim Nováček (1905–1942)<sup>4</sup>, who made important contributions to the knowledge of the mineralogy of uranium.

The first specimen was labelled uranospinite, which is the calcium uranyl arsenate member of the autunite group. It comprised a small piece of deeply altered, quartzose and limonite vein material that was coated and veined by secondary uranium minerals. The so-called uranospinite was present as a small area, apparently a filled cavity, of a platy, cleavable mineral of a straw-yellow color. This was subsequently identified as novacekite. The substance closely resembles saléeite in general appearance. It forms lamellar and sub-parallel aggregates of small plates with a perfect basal cleavage. The specific gravity is 3.6. Small irregular flakes of zeunerite were present around the borders of the mass of novacekite and represent the first deposition on the cavity walls. Small groups of crystals of zeunerite were present elsewhere on the specimen together with tufted crusts of uranophane and an impregnation of a golden-yellow, earthy uranium mineral that has not been identified. The amount of novacekite available on the specimen was insufficient for a quantitative analysis. A careful qualitative chemical examination of hand picked samples was made by Mr. F. A. Gonyer. This proved the substance to be a hydrated uranyl arsenate, with a strong trace of phosphate, but with calcium absent and with magnesium present in its place. The mineral is the arsenate analogue of saléeite and is isostructural therewith as shown by x-ray study described beyond.

The second specimen found of this mineral, from the Roebling collection of the U. S. National Museum, also was labelled uranospinite. This specimen comprised a small, friable mass of vein material, light brown in color and composed largely of limonite and quartz. The mass is somewhat fractured and the cavities are lined or filled completely by indistinct straw-yellow to lemon-yellow crystals of novacekite. Euhedral crystals are thick tabular on {001} and are rectangular in shape with rounded {h0l} forms and are not measurable. There is a perfect cleavage

<sup>4</sup> A memorial of Nováček is given by Čech: *Věstník Stát. Geol. Ústavu Republiky Českoslov.*, **20**, 23 (1945).

on {001}. The luster is weak, inclining to waxy. The hardness is  $2\frac{1}{2}$  and the specific gravity 3.25. The veinlets are bordered by green crystals of zeunerite, which formed earlier than the novacekite, as in the first specimen described, and some of the novacekite crystals show intergrown cores of zeunerite in parallel orientation. The zeunerite has  $n_O=1.637$ ,  $n_E$  1.620, and is not quite uniaxial ( $2V=0^\circ$  to about  $8^\circ$ ). Sufficient novacekite was available on the specimen for a complete analysis (column 5, Table 2). This proved the material to be a hydrated magnesium uranyl arsenate-phosphate, conforming to the autunite formula-type, with arsenate and phosphate substituting mutually almost in equal amounts.

*X-Ray Crystallography and Optical Properties.* The x-ray powder patterns of the two samples of novacekite described above differ from those of the pure saléeite from Portugal and Shinkolobwe, and of the arsenatian saléeite from Schneeberg (Columns 2, 3, 4 in Table 1) only in having slightly greater cell sizes. The tetragonal cell dimensions obtained from the powder patterns are cited in Table 2.

Optically, both samples of the Schneeberg novacekite are biaxial negative with  $2V$  ranging from nearly  $0^\circ$  up to about  $15^\circ$ . The phosphatian novacekite of analysis 5 in Table 2 shows mottled extinction with at times a parquet-structure on a fine scale. There was some variation in indices between different grains in both samples. The values cited in Table 1 represent the great bulk of the sample in the two cases. The variation in indices is doubtless due to variation in the content of zeolitic water within the stability range of the fully-hydrated phase. This feature and the appearance of biaxial characters within this range as a function of water content also occurs in other members of the autunite group, and in the meta-I hydrates as well, and has been discussed in light of the crystal structure by Beintema.<sup>2</sup>

Both the indices of refraction and the unit cell dimensions in general increase with increase in the ratio of As to P, as would be expected, but the variation shown is somewhat irregular. This can be ascribed to differences in the water content of the several samples that are independent of the As:P ratio. A more regular relation between indices and composition presumably would be obtained if all of the samples were hydrated to the same degree.

Saléeite free from arsenate fluoresces a bright lemon-yellow in both short-wave and long-wave ultraviolet radiation. The phosphatian novacekite of analysis 5 and the essentially pure arsenate end-composition fluoresce a dull green. The intensity of the fluorescence in all instances is somewhat less in short-wave than in long-wave radiation.

*Chemistry.* The available analyses of saléeite and novacekite are listed

in Table 2. The saléeite from Shinkolobwe and Portugal represents the pure phosphate compound. The Schneeberg material of analysis 4 is an arsenatian variety of saléeite with  $P:As=1:0.22$ ; the material of analysis 5 is a phosphatian variety of novacekite with  $P:As=1:1.01$ . A series involving mutual substitution of As and P in the formula  $Mg(UO_2)_2(P,AsO_4)_2 \cdot nH_2O$  thus extends from the pure phosphate end up to at least  $P:As=1:1$ . While material with larger amounts of arsenate has not been analyzed, qualitative tests show the existence in nature of the essentially pure arsenate end-member and the series probably is

TABLE 2. CHEMICAL ANALYSES OF SALÉEITE AND NOVACEKITE

	1.	2.	3.	4.	5.	6.
CuO					1.73	
PbO			0.21			
MgO	4.40	5.01	4.04	4.31	3.41	4.01
Al <sub>2</sub> O <sub>3</sub>			0.37			
UO <sub>3</sub>	62.41	64.07	63.05	60.32	59.74	56.96
P <sub>2</sub> O <sub>5</sub>	15.50	14.44	14.97	11.98	6.87	
As <sub>2</sub> O <sub>5</sub>			nil	4.50	11.23	22.88
H <sub>2</sub> O	17.69	16.48	17.42	[18.89]	[17.02]	16.15
Total	100.00	100.00	100.06	[100.00]	[100.00]	100.00
G		<3.3		3.27	3.3	3.6

1.  $Mg(UO_2)_2(PO_4)_2 \cdot 9H_2O$ . Theoretical composition.
2. Saléeite. Shinkolobwe, Belgian Congo. Mollet analysis of original material cited by Thoreau and Vaes (1932). Recalculated to 100 after deducting 2.79 per cent insoluble.
3. Saléeite. Sabugal, Portugal. H. J. Hallowell analysis, 1949.
4. Arsenatian saléeite. Schneeberg, Saxony. Gonyer analysis cited by Mrose (1950).
5. Phosphatian novacekite. Schneeberg, Saxony. Gonyer analysis, 1949. Recalculated to 100 per cent after deduction of insoluble  $SiO_2$  and  $Fe_2O_3$ .
6.  $Mg(UO_2)_2(AsO_4)_2 \cdot 9H_2O$ . Theoretical composition.

complete. The species name saléeite and novacekite are here applied to the halves of the series with  $P > As$  and  $As > P$ , respectively, in atomic per cent.

The novacekite of analysis 5 contains some Cu in substitution for Mg, with  $Cu:Mg=1:3.9$ , and indicates a series extending toward zeunerite. Qualitative tests on various specimens of uranospinite in the Harvard collection indicates that Mg is sometimes present in significant amounts in substitution for Ca and a partial series at least extends between this species and novacekite.

*Synthesis of Novacekite.* A rather flocculent precipitate found by qualitative test to be magnesium uranyl arsenate was obtained by reac-

tion at room temperature of water solutions of magnesium chloride, uranyl acetate and ammonium acid arsenate in the molar ratio of 1:2:2. The material gave a very diffuse powder pattern and was too fine grained for optical study. The precipitate was then heated at 50° in the mother solution for several weeks. The product gave a definite pattern that was similar to that of meta-autunite and which presumably represents the meta-I hydrate of novacekite. Optical data could not be obtained. Uranospinite is easily obtained in crystals by similar means.

*Occurrence of Uranium Arsenates and Phosphates.* The composition of the secondary uranium minerals formed by the alteration of uraninite in the zone of weathering is influenced by the nature of the primary minerals immediately associated with the uraninite. At Schneeberg, the presence of abundant arsenides of cobalt, nickel, and iron in the veins has resulted in the formation of uranyl arsenates in the oxidized zone. The known arsenates of uranium, zeunerite ( $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$ ), uranospinite ( $\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$ ), novacekite ( $\text{Mg}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$ ), troegerite ( $\text{H}_2(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$ ), and walpurgite ( $\text{Bi}_4(\text{UO}_2)(\text{AsO}_4)_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ ) all were first described from Schneeberg and the three last named species are known only from this place. The bismuth content of walpurgite and of the bismuth-uranium oxide uranosphaerite, the latter also known only from Schneeberg, has been derived from the association of native bismuth with the Co-Ni minerals. A number of secondary arsenates containing Ca, Co, Ni, Fe or Bi also occur at Schneeberg, among them erythrite, annabergite, roselite, pharmacosiderite, pharmacolite, agricolite and atelestite. Zeunerite occurs in very minor amounts at Tintic, Utah, where its arsenate content has been derived by the oxidation of enargite. In contrast to the relations at Schneeberg, the uraninite from hydrothermal veins containing sulfides but with little or no arsenides typically affords on oxidation the uranyl sulfates uranopilite, zippeite, johannite ( $\text{Cu}(\text{UO}_2)_2(\text{SO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ ), and also torbernite ( $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ), the copper content of the two latter minerals coming from sulfides such as chalcopyrite. The uraninite of pegmatites and of fluorite deposits of the Wölsendorf type generally affords uranyl phosphates and silicates, such as autunite, phosphuranylite, uranophane, and beta-uranophane, in which the principal divalent cation is calcium. In these deposits, and in the uraninite-quartz-fluorite veins such as those of Portugal, sulfides are lacking and the cations, usually calcium but sometimes magnesium and aluminum, the latter appearing in sabugalite ( $\text{HAl}(\text{UO}_2)_4(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$ ), are probably derived locally in the zone of weathering from the alteration of the wall-rock or from fluorite or apatite. Torbernite does not occur in significant amounts in deposits of the latter type due to the general absence of primary copper-containing sul-



fides. Lead, however, sometimes is present, as in parsonsite, kasolite, and dewindtite, but probably is of radiogenic origin. The phosphate content of the secondary uranium minerals in these occurrences and probably also in the sulfide veins apparently is derived from associated apatite. This certainly is true of the pegmatite occurrences. The origin of the abundant phosphate in the oxidized uranium veins of the Belgian Congo is not clear, but probably has come from the dolomitic limestones of the country rock via meteoric solutions. In the absence of both phosphate and arsenate, the uraninite of sulfide veins alters chiefly to johannite, as in Gilpin County, Colorado, and to other sulfates, but these minerals are only sparsely developed due to their relatively high solubility. The uranyl carbonates, including schroeckingerite, bayleyite, andersonite, and swartzite, also are relatively soluble compounds and typically develop as efflorescences in the upper part of the oxidized zone. Oxidation at Great Bear Lake is only superficial and the principal secondary minerals are oxides of uranium and of uranium and lead with very minor amounts of zippeite, uranopilite, and traces of johannite. Uranium arsenates have not been reported here, although the primary minerals include arsenides of cobalt, nickel, and iron, but annabergite occurs in small amounts. The hydrated hexavalent uranium oxides in general represent the first stage of alteration of uraninite and antedate the formation of the secondary phosphates, arsenates, and silicates.

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# CRYSTAL STRUCTURE DETERMINATION FROM ROUGH INTENSITY RELATIONS

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## ABSTRACT

A method is described by means of which the most probable atomic locations in a crystal can be found through consideration of a few strong reflections. In the example cited, four potential arrays are determined. Through proper consideration of missing reflections, a unique solution is found whose parameters agree to within .02 of those determined by conventional methods. The method should also be useful for interpreting Patterson diagrams.

## INTRODUCTION

In crystal structure determinations one is faced with the problem of proposing a reasonable structure and proving by computation of structure amplitudes and electron density maps that it is consistent with experimentally observed diffraction amplitudes. Often, one has the opportunity of choosing the trial structure on a logical basis, such as suspected isomorphism with another material, knowledge of the structure and packing of molecules or radicals, suspicion that the structure is derivative from a known one, and the like. Too often, however, one must begin the tedious computations with no idea, as to what the arrangement might be. In such instances, any device which may give a hint as to the most probable atomic locations, particularly if it can be accomplished rapidly and easily, is a useful and valuable addition to the techniques available to investigators, even though the results will not always be as definite as in the example to be cited. It is with that philosophy in mind that the following method for the preliminary steps of structure determination is presented. The discussion applies only to crystals with symmetry elements which project as centers of symmetry.

The method described here is based on an idea used so commonly by structure investigators as to have become almost second nature. If a given pinacoid "reflection," 300 for instance, is very strong—especially, though not necessarily—if succeeding orders of this reflection decrease in intensity in an orderly manner, one feels reasonably certain that there are accumulations of scattering matter at  $x=0$ ,  $1/3$ ,  $2/3$ . This information forms a starting point in the construction of a trial structure.

The above described concept need not be confined to reflections of

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simple indices. Robertson and White,<sup>1</sup> for example, have shown that one can obtain information concerning two parameters, in projection, by constructing lines representing the positions of maxima and minima of several strong reflections. Intersections of these are the most probable atomic positions. Donnay<sup>2</sup> described a similar technique. What has apparently been overlooked is that weak reflections, particularly those of zero intensity can give additional information. It is the purpose of this communication to demonstrate the usefulness of missing reflections in eliminating ambiguous atomic arrangements obtained from strong reflections only, by outlining a complete structure determination. For completeness, the entire theory will be developed.

### THEORY

A reciprocal point,  $hk0$ , may be considered as having associated with it a cosine wave with a periodicity  $h$  in the  $a$  direction and  $k$  in the  $b$  direction. The distribution of electron density throughout the projected unit cell is determined by compounding the waves associated with all reciprocal lattice points. The amplitude of any individual wave is given in  $F_{(hk0)}$ . A large amplitude suggests either that there are heavy, controlling atoms separated by a distance which has a component normal to the wave front equal, or nearly so, to the wave length of the wave corresponding to  $hk0$ , or that there are groups of smaller atoms whose centers of gravity are separated by the same amount. In either case, there are accumulations of scattering matter whose centers of gravity are separated by approximately the wave length of the wave associated with  $hk0$ . In the centrosymmetrical case, the centers of gravity must necessarily lie on the center of symmetry or the center must bisect the distance between them. This means that the wave has either a maximum or a minimum at the symmetry center.

The wave associated with  $hk0$  can be represented by lines indicating the positions of the maxima. Since the origin may be either a maximum or a minimum, the positions of the minima must also be indicated. These are shown in Fig. 1 for 210, where the solid lines are maxima and the dotted, minima. If  $F_{210}$  is large, the probability is high that there are pairs of accumulations of scattering matter separated by an integral number of wave lengths and lying near either set of lines. Assume a second reciprocal lattice point,  $\bar{1}30$ , whose amplitude is also large. The maxima and minima of its wave are shown in Fig. 2 superimposed on those of 210. Since the probability is high that there are accumulations of scatter-

<sup>1</sup> Robertson, J. M., and White, J. G., *Jour. Chem. Soc.*, **607** (1945).

<sup>2</sup> Donnay, J. D. H., Joint Meeting Crystallographic Society of America and American Society for X-Ray and Electron Diffraction, New Haven Conn., March 31-April 3, 1948.

ing matter along the lines representing both 210 and  $\bar{1}30$ , it is obvious that the probability is highest at the intersections of the two sets of lines. Clearly, the addition of the traces of the maxima and minima of the waves of additional strong points, particularly of low index, will further define the most probable atomic locations. However, there will, in general, be more than one possible array. A study of missing reciprocal lattice points frequently reduces the number.

The absence of a reciprocal lattice point implies destructive interference of the diffracted radiation arriving at that point. This means that there are centers of gravity of scattering matter separated by distances having components equal to an integral number of half wave lengths in

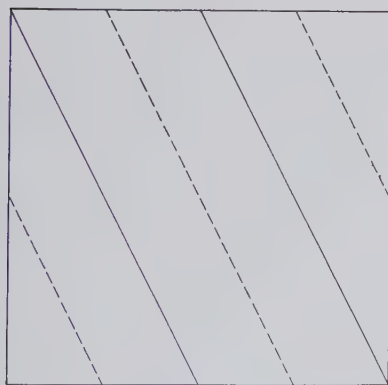


FIG. 1. Traces of the maxima and minima of the wave associated with 210.

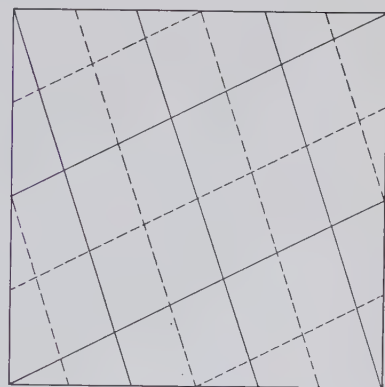


FIG. 2. Traces of the maxima and minima of the waves associated with 210 and  $\bar{1}30$ .

the direction normal to the wave front associated with the reciprocal lattice point. An even number of half wave lengths is possible only if the atoms lie along lines of zero amplitude. In other positions, each atom must have a centrosymmetrical equivalent separated from it by an odd number of half wave lengths in order for destructive interference to result. Atoms separated by an odd number of half wave lengths may lie along lines of zero, maximum or minimum amplitude since the conditions for destructive interference will always obtain. It is to be noted that, for each atom along a maximum, there will be a compensating one along a minimum.

#### EXAMPLE OF DETERMINATION OF ATOMIC POSITIONS

As an example of the use of the above described method, the most probable locations of the heavy atoms in lead chromate will be deter-



mined. The structure of lead chromate has been investigated by Brody<sup>3</sup> who found the following parameters for lead and chromium:

	$x$	$y$	$z$
Pb	0.220	0.150	0.400
Cr	.215	.150	.896

The four strongest reciprocal lattice points in the  $h0l$  series are 200,  $\bar{1}03$ ,  $\bar{2}02$ , and 204. Figure 3 shows the traces of the maxima and minima of the cosine waves associated with these points. Probable atomic locations are indicated by circles; these are the regions where maxima or minima of all four waves either intersect or cooperate strongly.

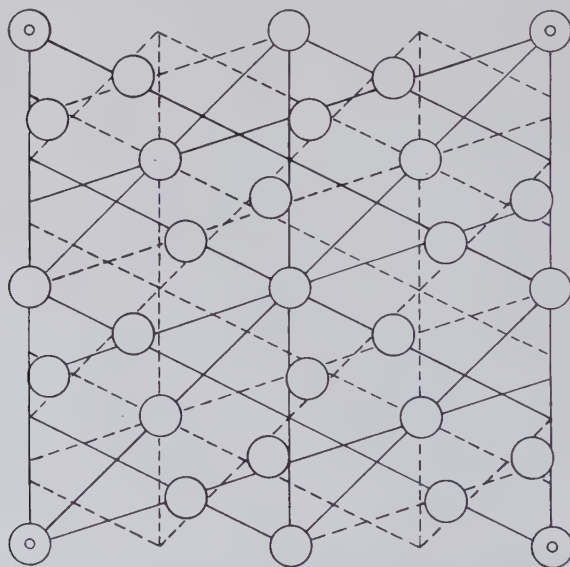


FIG. 3. Traces of the maxima and minima of the waves associated with 200,  $\bar{2}02$ ,  $\bar{1}03$ , 204. Circles represent probable locations of the heavy atoms in  $\text{PbCrO}_4$ .

It would appear from Fig. 3 that there is a large number of possible atomic arrangements. However, symmetry requirements reduce the number to a few possibilities. Lead chromate has the symmetry of the space group  $P2_1n$ . The  $h0l$  projection is centrosymmetrical and the parameters of the general position are  $x, z; \bar{x}, \bar{z}; 1/2+x, 1/2+z; 1/2-x, 1/2-z$ . Since there are four formula weights of  $\text{PbCrO}_4$  per unit cell, each real peak must generate three others by symmetry operations. (It is assumed that there are no coincidences of superimposed atoms in the projected cell.

<sup>3</sup> Brody, S. B., *Jour. Chem. Phys.*, **10**, 650 (1942).

This is true in the present example, but in general it must not be assumed.) Applying these symmetry conditions, it is found that there are eight independent groups of the locations shown in Fig. 3. Four of these contain only two atoms per cell and may be discarded under the conditions noted above. The remaining four are shown in Fig. 4 (*A* through *D*).

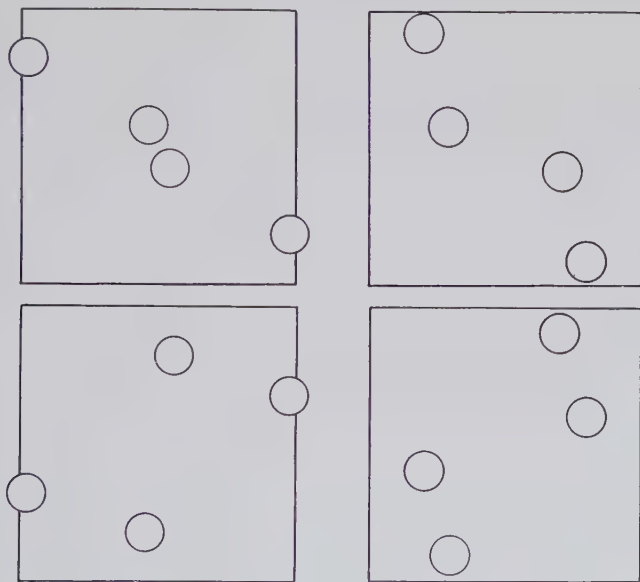


FIG. 4A-4D. Possible arrays of atomic positions in  $\text{PbCrO}_4$ .

Each array in Fig. 4 represents an atomic distribution for which the amplitudes of the reciprocal lattice points,  $200$ ,  $\bar{1}03$ ,  $\bar{2}02$ , and  $204$  will be large. Since there are two species of heavy atoms present, the correct atomic distribution will be represented by a combination of two of the arrays. In order to select the proper combination, we may now consider weak and missing reciprocal lattice points.

The proper combination of the maps of Fig. 4 will have all of the atoms lying along the lines of zero amplitude for a missing reciprocal lattice point or there will be as many along the maxima as along the minima. (The assumption is here made that the two atomic species have the same scattering power. Obviously they do not, but the approximation is useful.) By considering several missing reflections, it should be possible to reduce the various combinations of the maps to a number that can be handled easily.

In the case of lead chromate, the missing points of the  $h0l$  series include

the following:  $\bar{5}01$ , 202, 406, and 105. Traces of the maxima and minima of the waves associated with these points are shown in Fig. 5. Only half of the cell is illustrated. Also in Fig. 5 are the most probable atomic locations determined previously. They are labelled according to which of maps of Fig. 4 they correspond. Thus A 1 and A 2 are the symmetrically related peaks in the left half of Fig. 4A.

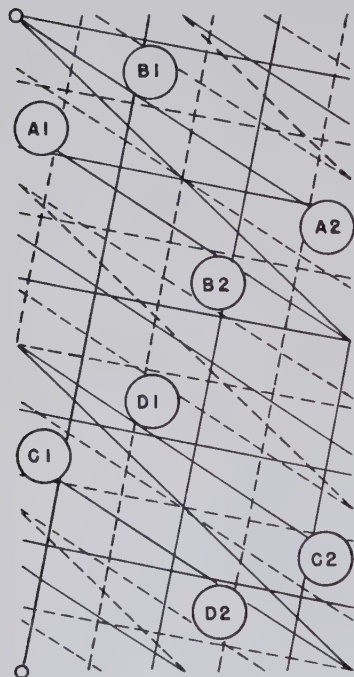


FIG. 5. Traces of the maxima and minima of the waves associated with  $\bar{5}01$ , 202, 105, and 406, showing the relation of amplitudes to probable atomic positions. (One-half the unit cell.)

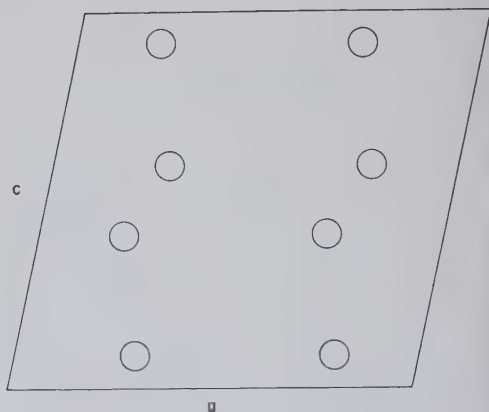


FIG. 6. Most probable structure of  $\text{PbCrO}_4$ .

Figure 5 may be analyzed by tabulating for each wave what locations lie near maxima, minima, and zero. A possible combination is one for which all atoms lie near zero or for which there are as many near maxima as near minima. All others can be discarded as unlikely. Analysis of Fig. 5 is given in Table 1.

Consider first the wave associated with  $\bar{5}01$ . It is apparent from Table 1 that combinations which satisfy the conditions can be formed in the following manner:

TABLE 1. RELATION BETWEEN ATOMIC POSITIONS AND AMPLITUDES OF WAVES OF MISSING RECIPROCAL LATTICE POINTS

<i>Point</i>	<i>Maximum</i>	<i>Minimum</i>	<i>Zero</i>
501	B 1	A 1	None
	B 2	A 2	
	C 1	D 1	
	C 2	D 2	
202	None	None	All
105	A 1	C 1	B 1
	A 2	C 2	B 2
			D 1
			D 2
406	A 1	None	B 1
	A 2		B 2
	C 1		D 1
	C 2		D 2

The maps of Fig. 4 may be combined, in pairs, in the following ways:

A+B  
A+C  
A+D

B+C  
B+D

C+D

B 1, B 2 and either A 1, A 2 or D 1, D 2 and C 1, C 2 and either A 1, A 2 or D 1, D 2. Combinations B 1, B 2 plus C 1, C 2 and A 1, A 2 plus D 1, D 2 can be eliminated, since all scattering matter would be concentrated along either maxima or minima. For 202, all combinations are possible because all positions lie near lines of zero amplitude. The other two waves can be analyzed similarly, and the results are given in Table 2. Since only the combination B+D satisfies the conditions for all four waves, it may be concluded that the most probable arrangement of the heavy atoms in lead chromate is that represented by the positions B and D. This combined array is shown in Fig. 6.

TABLE 2. MAP COMBINATIONS WHICH SATISFY CONDITIONS FOR MISSING RECIPROCAL LATTICE POINTS

<i>Point</i>	<i>Combination</i>					
	A+B	A+C	A+D	B+C	B+D	C+D
501	X	X			X	X
202	X	X	X	X	X	X
105		X			X	
406					X	



It is, of course, impossible to read accurate parameters from Fig. 6. However, crude values, representing the centers of the circles, can be refined by structure amplitude computations. Such rough parameters are listed in Table 3 along with the actual values found by Brody.

TABLE 3. COMPARISON OF ROUGH PARAMETERS FROM FIGURE 5  
WITH VALUES REPORTED BY BRODY

<i>Location</i>	<i>Parameters</i>				<i>Species</i>
	Figure 6		Brody		
	<i>x</i>	<i>z</i>	<i>x</i>	<i>z</i>	
B 1	.20	.91	.215	.896	Cr
B 2	.29	.58	.285	.604	Cr
B 3	.80	.09	.785	.104	Cr
B 4	.71	.42	.715	.396	Cr
D 1	.21	.42	.22	.40	Pb
D 2	.30	.09	.28	.10	Pb
D 3	.79	.58	.78	.60	Pb
D 4	.70	.91	.72	.90	Pb

#### ANALYSIS OF PATTERSON VECTORS

In the preceding example, potential atomic positions were found to fall into four patterns which, when properly combined in pairs, give a composite pattern consistent with the structure determined by conventional methods. In general, analysis of the various maps will not be so simple. The well known Patterson vector diagram will be of aid in choosing the most likely map, since the vectors of the arrangement chosen must appear on the Patterson diagram. Inconsistent maps and combinations can thus be eliminated.

One may go even farther and, in many cases, actually construct a map of potential atomic positions corresponding to a particular Patterson vector. In the Patterson diagram, the direction and magnitude of an interatomic distance vector is known but, in general, the locations of the ends of the vector are unknown. Following the reasoning developed above, one can say that it is highly probable that the atoms which form the ends of the vector lie on or near maxima (or minima) of those waves of large amplitude whose wave lengths are approximately equal to the component of the vector in the direction normal to the wave front.

To determine potential sites for the atoms which produce the vector, one selects the strong reciprocal lattice points for whose waves the vector has the correct component. Maxima and minima of the waves may be plotted as before, and maps of possible atomic arrangements obtained. A simple and rapid method of accomplishing the selection is to prepare

in advance, on tracing cloth, charts with lines representing maxima and minima of all of the reciprocal lattice waves of the type  $hk0$ , similar to the transparencies prepared by Huggins<sup>4</sup> for Fourier synthesis. The vector may then be drawn from the origin of the unit cell and the tracings placed in register one at a time. Those for which the end of the vector lies near a maximum or a minimum are the ones desired for construction of the maps. Tracings of this type are useful also when the type of map described earlier is constructed. The appropriate ones may be laid one over the other in register on a viewing box, and the potential atom locations marked off on a separate tracing. The same charts can, of course, be used in analysis of the missing reciprocal lattice points.

#### NOTE ON THE DETERMINATION OF PHASES

In cases such as the example described in this report where a logical structure can be deduced and where one may feel reasonably certain that the elements of the structure so determined control the phases of the various reflections, information concerning phases of additional reflections can also be deduced. Thus, in the case of lead chromate, it is apparent that all of the heavy atoms lie near maxima of 400, minima of 004, 103, and 402. The sign of 400 should, therefore, be positive and those of the latter three negative. Any analysis of this type must be viewed with considerable caution, however, particularly for the weaker reflections.

#### CONCLUSIONS

A method has been described by means of which probable atomic positions in crystals can be obtained rapidly and easily. The information thus obtained should prove useful in the selection of a logical structure for computation of structure amplitudes. In some cases, as in the example presented, the actual structure can be obtained uniquely. In general, this will not be so and many possibilities will exist. The use of Patterson vectors will help the selection. Results will probably be poor when there are many atoms of nearly the same scattering power and when there is no great variation of intensities. Accuracy cannot, of course, be obtained by use of the method, nor can low scattering atoms be located. It is believed that the method may be useful, under proper conditions, in guiding the preliminary steps of structure determinations.

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<sup>4</sup> Huggins, M. L., *Jour. Am. Chem. Soc.*, **63**, 66 (1941).

# STYLOTYPITE, A DISCREDITED SPECIES\*

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## ABSTRACT

The evidence on which the validity of stylotypite as a mineral species rests is reviewed. Existing published data are shown to be unsatisfactory, and attempts to verify reported occurrences of the mineral had negative results. All reported specimens of stylotypite which it was possible to identify are tetrahedrite or other known minerals. In the absence of valid data justifying stylotypite as a species, it should be discredited.

## INTRODUCTION

A previously accepted mineral species may become discredited in various ways, such as by proof that the type material was some other species, or that it was a mixture. Sometimes re-examination of the original material is not possible; but if the work done on the material is shown to be unsatisfactory and further, if no proven specimen of the alleged substance has ever been found—all alleged specimens being identified as other well-known species—then there are valid grounds for discrediting the supposed species. Such is the case with stylotypite, since 1865 accepted, with, it is true, occasional misgivings, as a mineral species. Since the original work by von Kobell almost a century ago, a score, more or less, of mineralogists have had to deal with this mineral and with few exceptions, have accepted without question the dubious statements of their predecessors. Not until 1931 was it shown by Schneiderhöhn and Ramdohr (1) that serious question existed as to stylotypite being a mineral species. However, stylotypite is still listed as such in several standard mineralogical text books.

## HISTORY OF THE MINERAL

The history of stylotypite is indicated in the chronological table shown on the following pages.

The name "stylotyp" given by von Kobell (2) is the Greek  $\sigma\tau\lambda\omicron\varsigma$  = column, and  $\tau\upsilon\pi\omicron\varsigma$  = form. The Spanish term canutillo was found on the label of the original specimen from Copiapo, Chile, in the collection of the Duchy of Leuchtenberg, signifying a small tube or pipe and refers to the shape of the material. Even in this original account, it was noted that except for its four-sided, almost rectangular ( $92\frac{1}{2}^\circ$ ) prismatic shape, it completely resembled tetrahedrite, and von Kobell's detailed account of the chemical and physical properties ends with the statement that (only) the external form of the material distinguishes it from tetrahedrite. Ap-

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TABLE 1. HISTORY OF "STYLOTYPITE"  
(Asterisk indicates first-hand study)

Year	Writer	Reference	Locality	Work
1865*	von Kobell, Franz	2	Copiapo, Chile	Proposed as species; made analyses
1892–1914	Dana, <i>System</i> , 5th and 6th Ed.	3		Listed as species
1898	Sommerblad, H.	4		Obtained synthetic $3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ . Did not name it
1903*	Stevanovic, S.	5	Copiapo, Chile Costrovirroyna, Peru	Measured crystals; made analyses
1908	Groth, Paul	6		Accepted stylotypite as species; discussed relationships
1909	Dana, E. S., and Ford, W. E.	7		Indicated similarity to falkenhaynite
1912	Parravano, N., and de Cesaris, P.	8		Termed synthetic $3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ stylotypite (instead of tetrahedrite)
1916	Murdoch, J.	9		Listed as species
1920	Davy, W. M., and Farnham, C. M.	10		Listed as species (very rare)
1921	Wherry, E. T., and Foshag, W. F.	11		Listed as species
1925*	Hulin, C. D.	12	Randsburg, Calif.	Identified stylotypite
1926	Doelter, C., and Leitmeier, H.	14		Accepted as species requiring further work
1931*	Schneiderhöhn, H., and Ramdohr, P.	1	Chile, Peru	Showed Stevanovic's 1902 work was done on mixture
1939	Gaudin, A. M., and Dicke, G.	15		Synthesized tetrahedrite but found no stylotypite in system $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$
1941	Strunz, H.	16		Listed as "tetrahedrite probably pseudomorphous after pyrostilpnite (?)"
1944	Palache <i>et al.</i>	17		Listed as species
1948	Klockmann-Ramdohr	18		Status of Peruvian stylotypite (1902) questioned as probably tetrahedrite
1949*	Milton-Axelrod	This paper		California "stylotypite" (1925) found to be tetrahedrite
1949*	Milton-Axelrod	This paper		Bolivian "stylotypite" found to be jamesonite, tetrahedrite, etc.
1949*	Milton-Axelrod	This paper		Peruvian "stylotypite" found to be tetrahedrite



parently, however, this was considered sufficient to give it species rank, and von Kobell's original questionable decision later found support in the even more questionable work of Stevanovic, cited below.

Von Kobell analyzed a specimen of his type material (Analysis *A*, Table 2). His work was repeated on similar material also from Copiapo, Chile, by Stevanovic (5) (Analysis *B*, Table 2). Further analytical work, also by Stevanovic, on "Stylotypite" from Peru, is given in Analyses *C*, *D*, *E*, and *F*, Table 2. This seems to be the total of all reported analyses of this substance.

Stevanovic noted that his Analyses *C*, *D*, and *E* of the Peruvian material are not in good agreement, especially *E*, and recognized this as proof of the heterogeneity of the analyzed material, notwithstanding its seeming homogeneity. Discussing the composition of the material, he ruled out tetrahedrite, which it indeed resembled, because of its darker color and easier solubility in acids—criteria of dubious significance—and also because of its crystallographic characters, of which more below.

He compared the Peruvian "stylotypite" with von Kobell's originally so-named material from Copiapo in Chile. It appeared identical with the Peruvian specimens, and, like these, gave discordant results on repeated analyses (*A* and *B*). He also analyzed a substance of somewhat similar composition, termed falkenhaynite by Scharizer, (20) which, after variously ascribed relationships, is now listed in the new Dana (17) as a discredited or doubtful species referred to the tetrahedrite series.

TABLE 2. ANALYSES OF "STYLOTYPE"

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>
S	24.30	23.12	23.20	23.20	25.75	24.55
Sb	30.53	28.58	22.15	26.31	16.86	18.99
As	—	—	6.20	4.32	6.28	7.07
Bi	—	—	1.12	1.12	.73	.54
Cu	28.00	30.87	41.50	36.05	43.60	45.84
Ag	8.30	10.43	1.40	1.34	1.44	1.62
Fe	7.00	6.27	2.24	2.76	3.98	—
Zn	tr.	tr.	1.54	3.43	.80	.90
Insol.	—	—	.34	1.41	.41	—
	98.13	99.27	99.69	99.94	99.85	99.51

*A* Copiapo, Chile, von Kobell, analyst.

*B* Copiapo, Chile, Stevanovic, analyst.

*C*, *D*, *E* Caudalosa, Costrovirroya, Peru, Stevanovic, analyst.

*F* *C* with 10.84% CuFeS<sub>2</sub> deducted.

Stevanovic found that the bulk of the Copiapo, Chile, "stylotypite" which he analyzed was not measurable goniometrically, because alteration had roughened the exterior of the nearly rectangular prismatic crystals. However, he found with this material a few crystals of different habit, two of which were "mechanically freed from their rough surface, and *polished with emery and buckskin*." A set of measurements (to seconds of arc) was obtained, and combined with measurements (not given) on "stylotypite from Caudalosa." However, he mentions that all the crystal faces were strongly striated, giving poor reflections. From such data Stevanovic computed axial ratios, etc., and deduced an isomorphous relationship between:

Xanthokon	$\text{Ag}_3\text{AsS}_3$
Feuerblende (pyrostitpnite)	$\text{Ag}_3\text{SbS}_3$
Stylotyp	$(\text{Cu, Ag, Fe/2, Zn/2})_3(\text{Sb, As, Bi})\text{S}_3$

In summary, both the chemical analyses and the goniometric measurements of von Kobell and Stevanovic are unsatisfactory and give no sound basis for considering the material studied to be a valid mineral species. Subsequent workers, with the few exceptions noted, appear to have accepted the original data; e.g., the latest edition of Dana (17) shows stylotypite listed as a species of composition  $(\text{Cu, Ag, Fe})_3\text{SbS}_3$ .

The older literature and data therein cited include crystallographic measurements by Stevanovic on material from the Caudalosa mine, Costrovirroya, Peru; this was later shown by Schneiderhöhn and Ramdohr (1) to be a mixture of a mineral in all respects like tetrahedrite, together with pyrite, enargite, and possible wittichenite, etc.

Sommerblad (4) obtained a compound of formula  $\text{Cu}_3\text{SbS}_3$  by fusion of copper chloride with antimony sulfide; its density was 5.182. That of a similar compound made from copper sulfide and antimony sulfide was 5.113. He noted that a cuprosulfantimonite of formula  $\text{Cu}_3\text{SbS}_3 (= 3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3)$  corresponding to (trigonal) pyrargyrite  $\text{Ag}_3\text{SbS}_3$ , does not occur in nature. Groth (6) discussing the orthosulfarsenic and orthosulfantimonic salts of univalent metals, noted that they form isodimorphous groups, the so-called ruby silvers of trigonal and a less common monoclinic symmetry; the latter is represented by stylotypite, essentially  $\text{Cu}_3\text{SbS}_3$ , with antimony partly replaced by arsenic, and copper by silver. It is, according to Groth, isomorphous with xanthoconite and pyrostitpnite.

Numerous other investigators have studied the system  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ , in particular Parravano and de Cesaris (8). They found two maxima on the fusion curve, one at  $542^\circ$  corresponding to  $\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$  or  $\text{CuSbS}_2$  (chalcostibite), the other at  $607^\circ$  corresponding to  $3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$  or

$\text{Cu}_3\text{SbS}_3$  ("stylotypite"). This may have been properly tetrahedrite, for all evidence to the contrary. Murdoch (9) listed stylotypite as a species; he gave the properties of a "fairly reliable" specimen from an unstated locality. He noted that the color in polished section was "practically the same" as (associated) tetrahedrite.

Davy and Farnham (10) in their textbook listed stylotypite as a "very rare" species.

In 1921, Wherry and Foshag (11) also accepted "stylotypite" as a species, with monoclinic symmetry.

Doelter and Leitmeier (14) cited the analyses already given, with Stevanovic's crystallographic data, and remarked that further examination of the mineral was in order.

Gaudin and Dicke (15) synthesized chalcostibite and tetrahedrite, also famitinite ( $3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ ) as well as the simple sulfides from melts containing copper, sulfur, and antimony. They referred briefly to stylotypite, mentioning both von Kobell's discovery and that Schneiderhöhn considered the mineral to be a variety of tetrahedrite. They found that the only compound of composition  $\text{Cu}_3\text{SbS}_3$  formed in their synthesis was always isotropic, and it was termed by them tetrahedrite without question.

A recent textbook (18) referred to the stylotypite from the Caudalosa mine, Peru (page 347), as probably pseudomorphs, now tetrahedrite; and (on page 371) as possibly pseudomorphs after pyrostilpnite.

Some years ago we became interested in this questionable substance, and wrote letters of inquiry to various mineralogists who might have some available for study. Also, through the kindness of Dr. Walter F. Hunt, a notice (19) of our interest was published, with no response. Only three mineralogists to whom we wrote had any, or knew where it might be obtained. Only three specimens labelled stylotypite turned up: in the collections of the National Museum, Washington, D. C., from the University of California, and one—the type Peruvian material—from the University of Freiburg in Breisgau, Germany. All of these have been studied by us, with results as follows:

#### "STYLOTYPE" FROM BOLIVIA

The first (C776) from the Canfield Collection now in the U. S. National Museum was labelled stylotypite, Machacamata (Machacamarca?), Bolivia. We have studied this, and find that the specimen consists of stubby prismatic crystals, and a massive mineral of similar lead gray color, showing a good conchoidal fracture. The two minerals have been respectively identified by *x*-ray study as jamesonite and tetrahedrite. Other ore minerals in subordinate quality can be seen microscopically.

The optical characteristics of this jamesonite differ somewhat from those stated in the literature, the mineral having lower birefringence than normal, and showing a slight development of twinning lamellae. Cleavage is not evident, and there is no "feathery" structure. The mineral is soft, with a brilliant "galena-white" reflection. J. M. Axelrod has identified the x-ray diffraction pattern as that of jamesonite. Further, Cyrus Feldman has analyzed the mineral spectroscopically, finding.

Major	Pb, Sb
Minor	Cu, Ag, Fe
Trace	Bi, As, B, Ni, V

The tetrahedrite was likewise identified by x-ray and spectroscopic studies showing:

Major	Cu, Sb, Ag
Minor	Zn, Fe
Trace	Bi, As, B, Ni

Optically, the tetrahedrite is normal—isotropic without cleavage. However, there are two varieties of two distinct shades of olive brown, the lighter more abundant, the darker occurring as inclusions in the first. Tetrahedrite often shows such variability.

Numerous tiny inclusions of chalcopyrite are present in the tetrahedrite, nearly always associated with equally tiny particles of a highly birefringent unidentified mineral.

Thus the Bolivian "stylotypite" is found to be a mixture, essentially of columnar jamesonite and massive tetrahedrite.

#### "STYLOTYPITE" FROM CALIFORNIA

The second specimen labelled stylotypite was obtained through the courtesy of Professor Carlton D. Hulin, who found it in the Rand silver mine, Randsburg, California (12). In a letter (13) to C. Milton, Professor Hulin stressed the tentative character of his identification, as necessarily resting on the mineralogical tables then available. The following quotations from his letter describe the occurrence, and supplement the published account:

"The determination (of stylotypite) was made about 1922-1923 at a time when the only mineral identification tables available for polished sections were those of Murdoch and Davy & Farnham. While the properties of the California Rand mineral reasonably satisfied the data given for stylotypite, considerable doubt naturally exists as to its true nature.

"In the California Rand ore the stylotypite lies between chalcopyrite and miargyrite-pyrargyrite-proustite in time—therefore forming at a



time when copper-iron-silver-antimony-sulphur might reasonably have been concurrently present in the mineralizing solutions. Remnants of chalcopyrite being replaced by stylotypite occur in moth-eaten patches resulting from replacement by miargyrite and pyrargyrite. The stylotypite characteristically was deposited in drusy cavities lined with quartz crystals, and overlapping the deposition of the quartz is itself usually filled with scattered tiny quartz crystals. These usually are torn out on polishing, leaving the "stylotypite" with a pitted surface.

"The stylotypite reacts with  $\text{HNO}_3$ , but is negative to other reagents used by Davy & Farnham. Hardness about 3 and apparently a little softer than tetrahedrite or chalcopyrite. Streak black. Color in polished section a faint pinkish-white or flesh color not unlike enargite or famatinite, but differing from those minerals in being apparently isotropic.

"I obtained definite qualitative microchemical tests for copper, silver, and iron on fragments gouged from the polished surface with a needle.

"I have a number of specimens of ore from the California Rand, but except in the polished surface the stylotypite is never apparent due to the varying degree of replacement by miargyrite, pyrargyrite, and locally other silver minerals, which is always shown."

X-ray study by J. M. Axelrod of the isotropic mineral gave the pattern of tetrahedrite. Spectrographic study of the same material by K. J. Murata showed:

Major elements	(>1%)	Sb, Cu, Ag, Fe, Si, Al, Pb
Minor elements	(.X%)	Mg, Ti
	(.0X%)	Zn, Ni, As, Sn, Mn, Ba, V
	(0.01%)	Au?
Not found		B, P, Sr, Mo, Be, Cb, Ta, Re, Y, La, Co, Bi, Ge, In, Se, Te, Hg, Pt, W, Zr

Evidently, then, Hulin's stylotypite is tetrahedrite.

Finally, Professor Hans Schneiderhöhn has generously permitted us to study the type "stylotypite" from the Caudalosa mine, Costrovirroy-na, Peru (Specimen No. 208, Mineralog. Inst., Freiburg) (1). X-ray study of this showed a pattern identical with that of tetrahedrite from various localities.

We are indebted to those mentioned above for having given us material for study or data concerning stylotypite. We are also indebted to F. A. Bannister, of the British Museum, C. Frondel, of Harvard University, F. H. Pough, of the American Museum of Natural History (New York), E. W. Nuffield, University of Toronto, Horace Winchell, Yale University, Vicente Juarez-Hoyos, Director of the Servicio Geologico Nacional, Bogota, Colombia, Robert Herzenberg, Oruro, Bolivia, Mark C. Bandy, Economic Cooperation Administration, Alfredo Garcia Stens, Banco

Minero del Peru, Lima, Peru, Juan Dalma, Regent of the National University of Tucuman, Argentina, Augustin Eduardo Riggi, Director General, Museo Argentino de Ciencias Naturales, Bernardino Rivadavia, Buenos Aires, Argentina, and F. Krantz, Bonn, Germany, all of whom kindly replied to our letters of inquiry, with negative results. This paper has been read and criticized by Michael Fleischer, George Faust, and Earl Ingerson.

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# A TEST OF THE PRECISION OF THIN-SECTION ANALYSIS BY POINT COUNTER

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## ABSTRACT

Five thin sections of granite from Westerly, Rhode Island, were analyzed by each of five relatively inexperienced operators using the point-counter method of determining the mode. Each operator ran his slides in a different sequence. In a preliminary run the observed analytical error for the constituents exceeded the expected error; in a second run by the same operators, now more experienced, the observed analytical error was approximately the same as the expected error. Evaluation of variances showed order of analysis to be insignificant throughout, operator and slide differences to be slight. The means for all constituents in both runs were remarkably close to the means previously obtained by Chayes in an independent run on the same sections. The test definitely establishes the level of precision for the point-counter method of analysis on a broader base than was possible from Chayes' unchecked analyses. The convenience and rapidity of the method are already well known; its precision has now been thoroughly tested.

The point counter described in this journal some time ago (Chayes, 1949) is now rather widely used and its popularity seems to be increasing steadily. The only published test of the precision of the method, that which accompanied the original description of the instrument, contained no information at all about interoperator differences, for the reason that at that time there were no other operators. In general, results obtained by different operators may disagree because of differences in identification or tabulation conventions, or because of differences in technique or competence. In the first case, and also where both types of difference are present, the results will be subject to a bias which varies from operator to operator. Where a difference in competence only is involved, the results are to be thought of as drawn from parent populations having the same means but different variances. We rarely have enough information to judge which type of difference is responsible for divergences between published results, and it is usually safe to assume the presence of both, as well as of some difference between samples.

It is pleasant to be able to report that the earlier precision test was apparently sound, that for major constituents the error attributable solely to the analytical process evidently is binomial,<sup>1</sup> as alleged, and,

<sup>1</sup> The "expected" or theoretical analytical error, as a number of points, is given by  $\sqrt{np(1-p)}$ , where  $p$  is the percentage of constituent and  $n$  the (total) count length. On a percentage basis this becomes  $\sqrt{p(1-p)/n}$ . The coefficient of variation, which is sometimes used as an index of relative error, is then  $C = \sqrt{(1-p)/np}$ .

most important, that interoperator differences can easily be held within reasonable limits. Results warranting these assertions have been obtained at Massachusetts Institute of Technology by a group consisting of C. K. Bell, W. H. Dennen, H. W. Fairbairn, M. L. Jensen, and F. B. Whiting.

A preliminary test was run by these analysts in May, 1950, using five thin sections cut from a single strip of Westerly granite. On a point counter similar to that in use at the Geophysical Laboratory each man analyzed each section once. The schedule followed by the analysts is shown in Table 1, in which the slides are identified by letters.

TABLE 1. SCHEDULE OF TEST

Order	1	2	3	4	5
Analyst I	A	B	C	D	E
II	E	A	B	C	D
III	D	E	A	B	C
IV	C	D	E	A	B
V	B	C	D	E	A

The results of this test were promising rather than satisfying. Agreement between the mean values obtained at MIT and at the Geophysical Laboratory was astonishingly good (see Table 2), and from this it was clear that there were no major identification biases. (The Geophysical Laboratory analyses were made some time before the test was started but the results were not known to any of the participants.)

Detailed examination of the results of the first run revealed some minor differences of opinion as to identification and some confusion about tabulation conventions. Finally, and most surprising in view of the excellent check of mean values, the observed analytical errors were significantly larger than predicted values for two of the three major constituents. (Compare rows 1 and 2 of Table 3.) These matters were discussed by the group and it was pointed out to them that the excess analytical error might be attributable to differences in both competence and learning rates, particularly the latter, if the practice period before the test had been inadequate.

Six months later the test was repeated with results shown in Tables 2 and 4B and in rows 3 and 4 of Table 3. In this run significant excess of observed over expected analytical error is not in evidence in the major constituents. It is still present in muscovite and for biotite it is larger in the second than in the first run. When results of the first test were compared with claims made earlier for the method (see Chayes, 1949, p. 7) it seemed entirely possible that the theory invoked seriously over-



TABLE 2. MEAN VALUES OBTAINED AT MIT AND GEOPHYSICAL LABORATORY\*  
(Volume Per Cent)

Mineral	Analyst Averages, MIT					Grand Means	
	I	II	III	IV	V	MIT	Geo-physical Laboratory
Quartz	26.1	26.2	26.3	27.8	27.3	26.8	27.1
	26.8	28.3	26.3	27.2	27.4	27.2	
Microcline	36.1	34.9	35.7	35.0	35.7	35.5	35.0
	35.0	35.0	35.7	35.9	34.5	35.2	
Plagioclase	32.4	33.7	32.7	29.7	30.7	31.8	32.2
	32.6	31.6	32.0	31.8	32.7	32.1	
Biotite	3.1	2.8	3.0	2.3	3.1	2.9	3.4
	3.3	2.8	4.1	2.7	2.9	3.2	
Muscovite	0.9	1.3	1.1	3.1	2.0	1.7	1.2
	1.2	1.3	1.1	1.0	1.3	1.2	
Opaques	0.8	0.7	0.8	1.0	0.9	0.9	0.7
	0.7	0.7	0.9	0.9	0.7	0.8	
Nonopaques	0.5	0.4	0.3	1.1	0.3	0.5	0.5
	0.4	0.3	0.2	0.6	0.5	0.4	

\* Upper entry at left is for first MIT test, lower entry on right for second.

estimated precision. For major and accessory constituents this possibility is clearly eliminated by the second test. It is probable, therefore, that with a little further practice this group of analysts would soon be obtaining results in accord with prediction for all constituents. The only remaining difficulty seems to be inability to stabilize identification conventions for the micas, and this difficulty may be anticipated whenever

TABLE 3. OBSERVED AND EXPECTED ANALYTICAL ERROR IN THE MIT TESTS\*  
(Per Cent of Whole)

Mineral	Quartz	Micro-cline	Plagio-clase	Biotite	Musco-vite	Opaque	Non-opaque
First Test							
Observed	1.3	1.4	1.1	0.4	0.4	0.2	0.2
Expected	0.88	0.96	0.93	0.33	0.26	0.18	0.14
Second Test							
Observed	1.0	1.1	0.9	0.6	0.4	0.1	0.1
Expected	0.89	0.96	0.93	0.35	0.22	0.17	0.12

\* See footnote 1.

biotite is partly replaced by chlorite and much of the muscovite occurs in minute flakes replacing plagioclase.

TABLE 4A. INDIVIDUAL RESULTS, FIRST MIT TEST  
(Volume Per Cent)

Analyst	Slide	Quartz	Micro- cline	Plagio- clase	Biotite	Musco- vite	Opaques	Non- opaques
I	A	25.7	35.8	33.3	2.6	1.2	1.0	0.4
	B	25.5	38.0	32.3	2.4	0.6	0.7	0.5
	C	26.8	35.4	31.8	3.6	0.8	1.0	0.6
	D	25.4	38.0	31.4	3.0	0.6	1.0	0.7
	E	27.0	33.4	33.2	3.9	1.3	0.5	0.6
II	A	24.8	35.0	34.4	2.9	1.6	0.7	0.5
	B	26.2	35.4	32.9	3.0	1.3	0.8	0.4
	C	26.2	35.7	34.0	2.4	0.8	0.7	0.2
	D	25.8	35.9	33.7	2.3	1.3	0.6	0.4
	E	28.1	32.5	33.3	3.2	1.7	0.7	0.5
III	A	24.6	36.5	33.3	3.4	1.3	0.6	0.3
	B	25.7	35.2	33.7	3.2	1.2	0.8	0.2
	C	27.2	36.6	32.0	2.7	0.4	0.9	0.2
	D	25.0	37.9	31.8	2.8	1.2	0.8	0.5
	E	29.2	32.3	32.7	3.0	1.2	1.0	0.5
IV	A	27.5	35.2	28.7	2.4	4.1	1.0	1.1
	B	28.4	34.2	30.3	2.6	2.9	0.8	0.8
	C	28.2	35.1	29.8	1.7	2.4	1.6	1.3
	D	26.9	34.6	30.8	2.5	3.0	1.0	1.0
	E	28.0	35.9	28.7	2.5	3.1	0.8	1.0
V	A	29.0	33.9	29.8	3.7	2.5	1.0	0.2
	B	26.5	38.2	30.2	2.7	1.3	0.6	0.4
	C	27.5	36.5	29.8	2.6	2.4	1.0	0.4
	D	28.2	35.2	30.2	3.0	1.9	1.1	0.4
	E	25.4	34.9	33.3	3.6	1.8	0.9	0.1

A brief note on analytical error may be helpful to some readers. It is important to remember that this error has nothing to do with mistakes or differences of opinion about identification, and expresses uncertainty inherent in the method under optimum circumstances. On the assumption that all five operators are competent and that each is using a stable set of identification conventions, the schedule of calculations is such as to throw differences ordinarily regarded as "mistakes" into the operator and slide variances (see Table 5). The remaining (analytical error)

variance then expresses the failure of all results to agree exactly *after due allowance has been made for differences between both slides and operators*. It is part of the method, and if uncertainty arising from it is too large for comfort this uncertainty can be reduced only by extending the count length (e.g., reducing the vertical or horizontal distances between clicks) or by resorting to replicate analyses. For the individual worker the first of these alternatives is always preferable because the number of random replications which can be made on the same slide by the same operator-instrument combination is very small, and nothing is gained by retracing one's steps exactly.

If the error of the method is actually binomial, as alleged, entries in

TABLE 4B. INDIVIDUAL RESULTS, SECOND MIT TEST  
(Volume Per Cent)

Analyst	Slide	Quartz	Micro- cline	Plagio- cline	Biotite	Musco- vite	Opakes	Non- opakes
I	A	24.7	35.6	33.3	3.3	2.0	0.6	0.6
	B	26.8	35.7	32.6	3.5	0.4	0.6	0.4
	C	28.0	34.2	32.1	3.4	1.1	0.7	0.4
	D	27.8	35.0	31.5	3.3	1.0	0.9	0.5
	E	26.6	34.5	33.6	3.0	1.4	0.6	0.3
II	A	27.3	35.5	32.1	2.5	1.5	0.8	0.3
	B	27.3	35.4	31.7	3.4	1.4	0.6	0.1
	C	28.0	35.3	31.1	2.8	1.4	0.8	0.5
	D	30.1	33.8	31.5	2.6	0.9	0.7	0.2
	E	28.7	35.2	31.4	2.6	1.3	0.6	0.2
III	A	25.8	36.0	33.5	2.9	0.8	0.7	0.3
	B	25.5	33.9	33.7	4.9	0.8	1.0	0.1
	C	26.1	37.8	30.7	3.4	1.1	0.7	0.3
	D	26.2	36.0	29.5	5.7	1.3	1.1	0.1
	E	27.8	34.7	32.4	3.6	0.7	0.8	0.2
IV	A	26.4	36.2	32.7	2.1	1.1	0.8	0.6
	B	26.6	36.3	31.9	3.2	0.8	0.6	0.7
	C	28.1	36.4	30.6	2.4	1.0	1.0	0.6
	D	27.1	35.9	31.6	2.7	0.9	1.1	0.6
	E	28.0	34.6	32.2	3.0	1.0	0.8	0.4
V	A	25.2	34.1	34.9	2.6	1.8	0.7	0.6
	B	28.6	34.5	31.6	2.7	1.6	0.6	0.4
	C	28.3	33.0	32.8	3.7	1.0	0.7	0.4
	D	26.3	36.1	32.3	2.9	1.1	0.8	0.5
	E	28.6	34.6	31.9	2.7	1.2	0.5	0.5

lines 2 and 4 of Table 3 are better estimates of it than either set of observed values, for they depend only on the grand mean for each constituent, and the error of this grand mean is small. Each operator's analyses should be approximately normally distributed around his own mean with  $\sigma$  equal to the appropriate entry in line 2 or 4 of Table 3. The frequencies of differences less than  $\sigma$ , intermediate between  $\sigma$  and  $2\sigma$ , and greater than  $2\sigma$  for the entire suite of analyses ought to be about in the ratio .65:.30:.05. For the set of 25 analyses of each constituent, there should be about 16 differences  $<\sigma$ , 7 or 8 in which  $\sigma<\Delta<2\sigma$ , and 1 or 2 which are larger than  $2\sigma$ . The observed differences for the two runs are

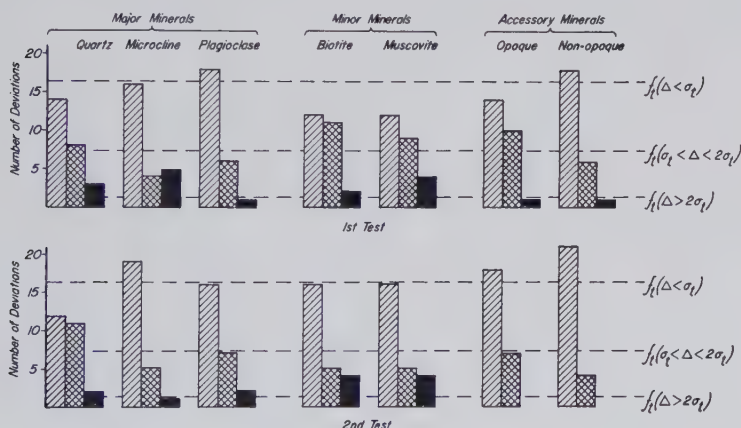


FIG. 1. Deviations of individual results from operator means. (For each constituent the bar at the left shows the number of deviations  $<\sigma_t$ , the center bar shows the frequency of deviations such that  $\sigma_t < \Delta < 2\sigma_t$ , and the bar at the right shows the frequency of deviations  $>2\sigma_t$ . The theoretical [normal] frequencies are shown by the dashed lines.)

calibrated in this fashion in Fig. 1 (the hundredths place was retained in the theoretical errors for this comparison); for each constituent the bar on the left gives the frequency of  $\Delta < \sigma$ , the center bar shows the frequency of  $\sigma < \Delta < 2\sigma$ , and the one on the right shows the frequency of  $\Delta > 2\sigma$ . In such small samples an exact check is not possible and even a close check is rather encouraging. With the exception of quartz differences, which are about the same in both runs, the second run shows considerable improvement over the first for essential minerals. It is rather curious to find that *least* difficulty was encountered with accessory minerals.

The full array of mean squares generated by the second run, calculated from the data of Table 4B and used in the variance analysis, is shown in Table 5. The discussion of the preceding paragraphs takes care of the



last two columns of the table so that only analyst and slide differences<sup>2</sup> remain to be noted.

No highly significant differences between slides have been established even though each slide has been analyzed five times. The slides are no doubt different, but the differences between them must be very small. There is some indication of small differences in quartz and plagioclase, but in both cases the *F* ratios are well below the .01 point.

Perhaps the most important result of the test is contained in the first column of Table 5. There seem to be no significant differences between

TABLE 5. MEAN SQUARES CALCULATED FROM TABLE 4B

Mineral	Source of Variation			(Theoretical Error) <sup>2</sup>
	Analysts	Slides	Error (Obs.)	
Quartz	2.7884*	3.3594*	0.8949	0.7921
Microcline	1.6316	0.4436	1.1204	0.9125
Plagioclase	1.2846	3.2476*	0.8164	0.8723
Biotite	1.6694**	0.6074	0.3259**	0.1224
Muscovite	0.1124	0.1784	0.1232**	0.0466
Opakes	0.0496*	0.0546*	0.0141	0.0298
Nonopaques	0.1246**	0.0226	0.0106	0.0155

\* See footnote 2.

analysts so far as plagioclase, microcline, and opaque accessories are concerned, and for quartz the *F* ratio is barely beyond the .05 level. If this *F* ratio is not itself in error, e.g., if it is not indicating a difference when none in fact exists, the variance components of quartz attributable to interanalyst differences may be estimated as 2.0455/5. Expressed as a standard deviation this comes to  $\sqrt{2.0455/5}$  or 0.6 per cent of the whole. As the mean quartz content is 27.2, the error component attributable solely to operator differences amounts to 2.2 per cent on a relative basis. The estimation of biotite by the group is probably still affected by incomplete standardization of tabulation procedures; at any rate, analyst difference is highly significant for biotite and nonopaques taken

<sup>2</sup> The object of the calculations—actually the object of the test—is to obtain estimates of variance which may be compared with each other. Identifying sources of variation by subscripts, the ratio  $F = V_a/V_e$  is a measure of the differences between analysts in terms of analytical error. Use of the *F* ratio and a tabulation of the .05 and .01 significance levels are given in many modern elementary texts (e.g., Snedecor, 1946, pp. 220–225 and accompanying discussion). A sample mean square yielding an *F* value exceeding the .05 point is customarily denoted by a single asterisk. One giving an *F* value exceeding the .01 point is denoted by a double asterisk. These conventions are followed in Table 5.

separately but only suggestive for the sum (biotite+nonopaques). Some of the analysts may be recording chlorite which replaces biotite partly under biotite and partly under nonopaques.

At the literal level the experiment may be dismissed as showing only that there are at MIT five petrographers who get about the same results as one petrographer at the Geophysical Laboratory. The design and execution of the test, however, justify more general inference. Viewing the results in the most favorable light, we may conclude that with reasonable care and practice there is no reason why the reproducibility of quantitative thin-section analysis should not easily equal that of analytical methods ordinarily regarded as inherently far more precise. The common practice of calculating norms or modes from chemical analyses is far more expensive and leads to results no more precise than those of thin-section analysis, providing, of course, that the material in question is neither glassy nor excessively coarse.

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SNEDECOR, G. W. (1946), *Statistical Methods*, Iowa State College Press, Ames, Iowa.

#### TECHNICAL NOTE

A study such as this offers nothing novel to the professional statistician, and in order to keep the discussion within bounds no attempt has been made to satisfy readers uninterested in or completely unfamiliar with statistical analysis. For this latter group the argument is necessarily one of example rather than precept; it will have been successful if it succeeds in whetting their appetites. Excellent descriptions of the experimental design and calculations will be found in Snedecor (1946, pp. 265-274) as well as in most other modern elementary texts.

Readers familiar with practical statistical work will have noted from Table 1 that the original test was set up in a Latin square. It was anticipated that significant operator biases would be found, but that the analysts would have sufficient opportunity for practice in advance of the test so that their improvement after its start would not be marked enough to influence the result. A significant mean square for order would thus imply instability which could not be attributed to learning or incompetence but would have to be regarded as one of the hazards of the method. The expected biases did not emerge in the first test; as has already been noted, however, this might have been because analytical error variances for essential minerals were all larger than anticipated. Although operator differences in the first run were not significantly larger than observed error variances, several of them *were* larger than the appropriate

theoretical error variances, and a more extensive test had already provided confirmation of the theoretical values.

Maximum interest in the second run therefore focused on the analytical error. In the first run the effect of "order" was negligible, and when this proved to be the case in the second also this criterion was abandoned. Its four degrees of freedom were pooled with the twelve allotted to "discrepance" in the original square, thus materially strengthening the test as a measure of analytical error. With elimination of one factor the Latin square degenerates into a randomized block design, and it is in this form that calculations from the final data are shown in Table 5.

The fact that the excess of analytical error noted for major constituents in the first run is not in evidence in the second implies that the basic assumptions required for proper application of the design were not valid when the test was begun. The simplest explanation is that the practice period preceding the test was not adequate and that some of the operators improved notably during the first run. This would find expression as an analyst-order interaction, and, in either the square or block design, variation occasioned by this interaction would enlarge the observed error variance. The plausibility of this explanation is considerably increased when it is recalled that of the four possible interactions the other three all involve the sections, and major mineral differences between slides have not been clearly established by either run. Interactions involving the slides should therefore all be negligible.

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# IGNEOUS ROCKS OF THE CAPITAN QUADRANGLE, NEW MEXICO, AND VICINITY

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## ABSTRACT

Igneous rocks are extensively exposed in the Capitan quadrangle, occurring in the mountain masses of Carrizo, Patos, Capitan, Vera Cruz, and Sierra Blanca Mountains, and in numerous dikes, sills and extrusions throughout the quadrangle.

This paper presents the results of quantitative mineralogical studies of igneous rocks from different parts of the quadrangle and from a few localities adjacent to it.

The Capitan quadrangle is in central New Mexico. It lies between the parallels  $33^{\circ}30'$  and  $33^{\circ}45'$  and the meridians  $105^{\circ}30'$  and  $105^{\circ}45'$ .

The Capitan Mountains extend into the east central part of the quadrangle and the Sierra Blanca enter it in the southwest. Carrizo and Patos Mountains occupy the northwest corner of the quadrangle, and the Vera Cruz Mountains are in the west central part.

Igneous rocks are found extensively in the quadrangle occurring in the mountain masses and in dikes, sills, and extrusive flows in different parts of the quadrangle.

This paper embodies the results of micrometric studies of the different igneous rocks of the quadrangle and vicinity.

In making these studies measurements were made by means of a Wentworth recording micrometer, fifteen traverses being made for each thin section. Universal stage methods were used in determining the plagioclase feldspars.

Rock classifications are according to Johannsen's system of quantitative mineralogical classification of igneous rocks.<sup>1</sup>

## PLUTONIC ROCKS

### *Modes of Kalialaskites*

	1	2	3	4	5
	%	%	%	%	%
Potash feldspar.....	71.2	75.2	71.5	72.6	80.4
Quartz.....	27.2	24.2	27.2	26.7	17.4
Magnetite and hematite.....	1.6	0.5	1.0	0.6	0.9
Biotite.....					0.8

<sup>1</sup> Johannsen, A. (1939), *Descriptive Petrography of Igneous Rocks*: Chicago, Univ. of Chicago Press.



	6 %	7 %
Potash feldspar . . . . .	88.3	83.0
Quartz . . . . .	8.1	16.5
Magnetite . . . . .	1.6	
Biotite . . . . .	1.7	
Hornblende . . . . .	0.3	
Dark constituents . . . . .		0.2

1. Center of NE  $\frac{1}{4}$  Sec. 25 T7S R14E, north side of Capitan Mountains.
2. Sec. 18 T8S R15E, southwest side of Capitan Mountains.
3. West side of pass through Capitan Mountains, east part of Capitan Mountains quadrangle.
4. Center of Sec. 25 T7S R14E, Capitan Mountains southwest of Encinoza.
5. Main ledge of west facing cliff of Vera Cruz Mountains.
6. Summit of White Mountain, Sierra Blanca southwest of quadrangle.
7. West end of Capitan Mountains, NE  $\frac{1}{4}$  Sec. 13 T8S R14E.

Modes of Alaskite

	1 %
Potash feldspar . . . . .	71.8
Quartz . . . . .	22.1
Dark constituents . . . . .	6.0

1. Gum Spring Canyon west central part of Capitan Mountains quadrangle.

Modes of Orthosites

	1 %	2 %	3 %
Potash feldspar . . . . .	95.0	91.2	91.7
Quartz . . . . .	3.6	3.8	3.7
Dark constituents . . . . .	1.2		
Biotite . . . . .		1.3	1.2
Oligoclase . . . . .		0.2	0.5
Hornblende . . . . .		1.9	2.5
Magnetite . . . . .		1.3	0.1
Apatite . . . . .		0.3	0.1

1. South side of Patos Mountain SW  $\frac{1}{4}$  Sec. 3 T7S R13E.
2. Sec. 30 T7S R13E. Powell Canyon, Carrizo Mountain.
3. NW  $\frac{1}{4}$  Sec. 19 T7S R13E. Base of cliff head of Powell Canyon, Carrizo Mountain.

HYPABYSSAL ROCKS  
*Modes of Kaliaaskite Porphyry*

	1 %
Potash feldspar.....	89.0
Quartz.....	8.9
Magnetite.....	1.8
Biotite.....	0.3

1. NE  $\frac{1}{4}$  Sec. 28 T9S R14E. Dike in bottom of small creek tributary to Salado Creek. This is representative of many dikes of the quadrangle.

*Modes of Diabase Porphyries*

	1 %	2 %	3 %	4 %	5 %	6 %
Labradorite.....	83.7	91.5	89.5	77.5	73.6	58.4
Augite.....	8.3	1.8	7.4	19.2	16.3	41.1
Chlorite.....	3.7	1.0	0.1	0.4	6.3	
Magnetite.....	4.3	5.2	2.7	2.6	3.8	9.5
Apatite.....		0.5	0.1			

1. SE corner of NW  $\frac{1}{4}$  of SE  $\frac{1}{4}$  Sec. 17 T8S R14E.
2. NE  $\frac{1}{4}$  of Sec. 29 T9S R13E.
3. Center of Sec. 31 T8S R14E, 2.4 miles northwest of Capitan on U. S. Highway 380.
4. SE  $\frac{1}{4}$  Sec. 31 T8S R14E, 2 miles northwest of Capitan on U. S. Highway 380.
5. Dike in valley of tributary to Aragon Creek NE  $\frac{1}{4}$  Sec. 22 T7S R14E.
6. NE  $\frac{1}{4}$  Sec. 8 TS9 R14E, 0.4 miles west of Capitan.

*Modes of Diabases*

	1 %	2 %
Labradorite.....	73.8	84.5
Chlorite.....	5.7	2.4
Augite.....	10.8	7.9
Magnetite.....		4.7
Hornblende.....	7.6	
Pyrite.....	1.8	
Illmenite, Magnetite and Leucoxene.....	0.3	

1. Dike south central border NW  $\frac{1}{4}$  Sec. 24 T8S R13E, one mile northeast of Indian Divide.
2. SE  $\frac{1}{4}$  Sec. 2 T9S R13E.

*Modes of Meladiabase*

	1 %
Labradorite.....	43.4
Augite.....	52.2
Magnetite.....	4.2

1. East part of Sec. 13 T7S R14E.

## EXTRUSIVE ROCKS

*Kalitordrillites*

A type of igneous rock occurring in this quadrangle is a very fine grained rock with practically no dark constituents. In thin section these rocks are seen to have the same minerals and in approximately the same proportion as kalialaskite. They are, therefore, classed as kalitordrillites, extrusive equivalents of kalialaskites.

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# THE IMPORTANCE OF EXCHANGEABLE MAGNESIUM AND CATION-EXCHANGE CAPACITY IN THE STUDY OF MONTMORILLONITIC CLAYS\*

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## ABSTRACT

In calculating the formulas of members of the montmorillonite group all the magnesium is generally assigned to the Al layer. However, determination of exchangeable cations in 14 montmorillonitic clays, 10 of them the identical specimens for which analyses were quoted by Ross and Hendricks (*U. S. Geological Survey, Prof. Paper 205-B*), showed that in all of them some of the magnesium was exchangeable, the amount ranging from 0.11 to 1.62 per cent. In two samples exchangeable magnesium amounted to about  $\frac{1}{3}$  of the total magnesium. These results indicate that the presence of exchangeable magnesium in the montmorillonitic clays is more common than is generally recognized.

Ross and Hendricks, assigning all magnesium to the Al layer in calculating the formulas of montmorillonites, found that the number of ions in octahedral coordination ranged from 2.02 to 2.24. However, a recalculation of the formulas of some of these samples on which exchangeable cations were determined showed that, when total magnesium is corrected for exchangeable magnesium and only non-exchangeable magnesium is assigned to the Al layer, and when the determined rather than an average cation-exchange capacity is used, the number of cations in octahedral coordination does not exceed 2.02, even in those samples in which the number of cations is as much as 2.13 when all the magnesium is assigned to the Al layer. Apparently, in montmorillonite then, substitution of Mg for Al in the Al layer is ion for ion, with no extra ions added in an effort toward internal compensation of charge.

By the Marshall method of calculation, the number of atoms in the octahedral layer in excess of 4.00, when all the magnesium is assigned to the octahedral layer, permits an estimation of the amount of exchangeable magnesium present and, from this, an estimation of the cation-exchange capacity of the sample. On the other hand, when only non-exchangeable magnesium is assigned to the octahedral layer, the number of atoms in this layer is very close to the theoretical 4.00, and the charge on the cell checks the charge of the external cations and the determined cation-exchange capacity, which it does not do when all the magnesium is assigned to the octahedral layer.

## INTRODUCTION

In the structural interpretation of analyses of clays of the montmorillonite group magnesium is generally assumed to be part of the crystal lattice and is assigned to the octahedral group, proxying aluminum. Calcium, sodium, and potassium are, on the other hand, thought to be too large to occupy positions in the crystal lattice without undue distortion of the lattice, and are, consequently, considered to be exchange cations, although potassium may be only partly replaceable. The possibility that magnesium may occupy exchange positions, as well as octahedral positions, thus playing a dual role, has been recognized, but generally neglected in interpreting the structure of these clays.

\* Published by permission of the Director, U. S. Geological Survey.



Of the cations commonly found in natural waters—calcium, magnesium, sodium, and potassium—magnesium ranks second only to calcium in replacing power.<sup>1</sup> Its superior replacing power as compared with that of sodium is indicated by the results obtained by Kelley and Liebig<sup>2</sup> on treating a bentonitic clay with sea water. Although sea water contains approximately 4.3 equivalents of sodium to 1 equivalent of magnesium, its action on a bentonitic clay, which had been converted to calcium clay before treatment with sea water, resulted in the replacement of somewhat more magnesium than sodium.

With few exceptions, natural waters contain some of all the common bases—calcium, magnesium, sodium, and potassium. When such a solution comes in contact with a cation-exchange mineral like montmorillonite, cations in the mineral are replaced by cations from the solution, the relative extent of replacement depending on the cations in the mineral at the time of contact, on the relative concentration of the cations in the solution, and on their respective replacing powers. As calcium is the predominant cation in most natural waters, and as calcium has the highest replacing power of the cations normally found in natural waters, it is not surprising that in naturally occurring montmorillonites calcium is generally the dominant exchangeable cation. But as most natural waters also contain some magnesium, and as magnesium ranks next to calcium in replacing power, it is to be expected that most montmorillonites would also contain some magnesium as an exchangeable cation.

In their comparison of the cation-exchange capacity of 22 samples of clays with the sum of the milliequivalents per gram of  $\text{Ca}^{+2}$ ,  $\text{Na}^{+1}$ , and  $\text{K}^{+1}$ , Ross and Hendricks<sup>3</sup> found that in nine of the samples the sum of these cations was considerably less than the determined cation-exchange capacity. In four of these samples alkalies had not been determined and there was the possibility that Na and K might account for the low summation, but in the other five samples the presence of exchangeable magnesium seemed a possible cause of the low summation. Even in those samples in which the sum of the milliequivalents of Ca, Na, and K equaled or exceeded the determined cation-exchange capacity the possibility of exchangeable magnesium was not to be ignored.

As several of the samples upon which Ross and Hendricks compared

<sup>1</sup> Schachtschabel, P., Adsorption by clay minerals, etc.: *Koll. Beih.*, **51**, 199–276 (1940).

<sup>2</sup> Kelley, W. P., and Liebig, G. F., Jr., Base-exchange in relation to composition of a clay with special reference to effect of sea water: *Am. Assoc. Petroleum Geologists, Bull.* **18**, no. 3, 358–367 (1934).

<sup>3</sup> Ross, C. S., and Hendricks, S. B., Minerals of the montmorillonite group: *U. S. Geol. Survey, Prof. Paper* **205-B**, p. 39 (1945).

cation-exchange capacity with the sum of the milliequivalents per gram of Ca, Na, and K had been analyzed in the laboratory of the U. S. Geol. Survey, it was possible for the author to obtain some of the identical materials for a study of exchangeable magnesium. Several other samples were supplied by Ross. Although these latter samples were from the same localities as some listed by Ross and Hendricks, reanalysis showed they were not identical. In all, 14 samples were obtained for the study. The source locality of these samples is shown in Table 1; those that are identical with the samples listed by Ross and Hendricks are identified by the use in the table of the same number as used by Ross and Hendricks. The study of these samples included, in addition to determination of exchangeable magnesium, determination of exchangeable Ca, Na, K, and H, total cation-exchange capacity, and water-soluble salts.

#### SOLUBLE SALTS AND CATION-EXCHANGE

Two-gram portions of the samples, ground to pass 80-mesh, were shaken with 200 ml of distilled water in a stoppered Erlenmeyer flask, allowed to settle overnight, the water decanted off through a filter paper, split into three portions, and Ca, Mg, Na, K,  $\text{SO}_4$ , and Cl determined. Material that had been transferred to the filter paper during the decantation was transferred back to the proper flask with a jet of distilled water.

After the samples were dried over a low steam bath, they were shaken with two successive 20-ml portions of normal  $\text{NH}_4\text{Cl}$  (neutralized), allowed to settle about 10 minutes, and the supernatant liquid decanted through a filter paper after each treatment. The samples were then washed with successive 20-ml portions of 95 per cent ethyl alcohol, decanting each portion through the filter paper, until the filtrate did not give a test for Cl with  $\text{AgNO}_3$ . The filtrates, consisting in each case of the  $\text{NH}_4\text{Cl}$  solution used in the treatments and the alcohol washings, were tested for acidity with a few drops of methyl red. The acidity of those filtrates which gave an acid reaction was determined by titration with 0.1 normal  $\text{Na}_2\text{CO}_3$ . The filtrates were then evaporated to dryness on a steam bath, the residue taken up with water slightly acidified with HCl, made up to volume and divided into two equal portions. On one portion  $\text{R}_2\text{O}_3$ , Ca, and Mg were determined; on the other  $\text{SO}_4$ , Na, and K. The final Na and K determination was made by means of a flame photometer. Material that had been transferred to the filter papers during the  $\text{NH}_4\text{Cl}$  treatments and the alcohol washings was washed back into the proper flask and the  $\text{NH}_4$  content of the treated clays was determined by distilling with 2 grams of  $\text{Ba}(\text{OH})_2$ , catching the distillate in a flask containing 50 ml of 2 per cent boric acid and a few drops of a (5-1) brom-

cresol green methyl red indicator.<sup>4</sup> After distillation of  $\text{NH}_4$  was complete, the amount of  $\text{NH}_4$  present in the distillate representing the total cation-exchange capacity of the sample was determined by titration with 0.1 normal HCl.

On several samples in which the dominant exchange cation was Na, it was not feasible to determine water-soluble salts by digesting the sample overnight with distilled water and filtering, because such samples settled so very slowly. On these samples Cl was determined by digesting a separate portion with water slightly acidified with nitric acid, filtering, neutralizing the filtrate with  $\text{CaCO}_3$ , and titrating it with standard  $\text{AgNO}_3$  solution. Sulfate was determined on all the samples on the filtrate from the cation-exchange treatment. Qualitative tests for  $\text{CO}_3$  on all the samples showed that only one sample, No. 12, contained  $\text{CO}_3$ .

#### DISCUSSION OF RESULTS

The sum of the milliequivalents per gram of the cations found in the cation-exchange filtrate minus the sum of the milliequivalents per gram of soluble anions and the resulting total, representing the cation-exchange capacities of the samples, are shown in Table 1, together with the determined cation-exchange capacities of the samples. For all the samples there is very good agreement between the determined cation-exchange capacity and the total cation-exchange capacity obtained by subtracting the sum of the milliequivalents per gram of the soluble anions from the sum of the milliequivalents per gram of the cations found in the cation-exchange filtrate. In most of the samples no soluble anions were found; the cations found in the filtrate from the cation-exchange treatment of these samples are apparently therefore all exchangeable cations, and the sum of their milliequivalents per gram represents the cation-exchange capacity of the sample. The only samples found to contain soluble anions were those in which Na is the dominant exchange cation. In these samples part of the cations found in the cation-exchange filtrate belong to the soluble anions found and the equivalent of these anions was subtracted from the sum of the cations to obtain the total of the exchangeable cations. The total thus obtained is in good agreement with the determined cation-exchange capacity for every sample in which soluble anions were found. In all these samples, however, the amount of soluble anions found was relatively small, indicating that by far the greater proportion of the cations found in the cation-exchange filtrate were exchangeable cations. As already pointed out, because of the colloidal na-

<sup>4</sup> Ma, T. S., and Zuazaga, G., Micro-Kjeldahl determination of nitrogen, A new indicator and an improved rapid method: *Ind. Eng. Chem., Anal. Ed.*, **14**, 280-282 (1942).

TABLE 1. EXCHANGEABLE CATIONS, SOLUBLE ANIONS AND CATION-EXCHANGE CAPACITIES OF SOME MONTMORILLONITE CLAYS

No.	Location	Cations				Soluble Anions		Total Cation- Exchange Milliequivalents per gram	Determined Cation- Exchange Milliequivalents per gram
		CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	H	CO <sub>3</sub>	SO <sub>3</sub>	
		Milliequivalents per gram					per gram		
3	Amargosa Valley, Calif.	[0.13+0.16+0.82+0.03+0.00]	minus	[0.00+0.01+0.03]	=		1.10		1.11
6	Tatavila, Mexico	[.83+.13+.00+.00+.00]	"	[.00+.00+.00]	=		.96		.98
10	Nieder-Bayern, Germany	[.59+.26+.00+.00+.00]	"	[.00+.00+.00]	=		.85		.86
12	Ardmore, S. Dak.	[.35+.08+.65+.02+.00]	"	[.11+.02+.00]	=		.97		.97
13	Irish Creek, Va.	[.77+.16+.00+.00+.00]	"	[.00+.00+.00]	=		.93		.94
14	Hector, Calif.	[.11+.06+1.06+.02+.00]	"	[.00+.04+.06]	=		1.15		1.15
20	Lemon, Miss.	[.44+.39+.00+.00+.06]	"	[.00+.00+.00]	=		.89		.89
22	Atzacapozalco, Mexico	[.24+.48+.12+.04+.00]	"	[.00+.00+.00]	=		.88		.88
24	Santa Rosa, Mexico	[.14+.80+.02+.01+.00]	"	[.00+.00+.00]	=		.97		.98
28	Greenwood, Maine	[.94+.08+.00+.00+.00]	"	[.00+.00+.00]	=		1.02		1.03
	Fort Steel, Wyo.	[.30+.26+.00+.00+.25]	"	[.00+.00+.00]	=		.81		.80
	Pala, Calif.	[.36+.59+.02+.00+.00]	"	[.00+.00+.00]	=		.97		.98
	Belle Fourche, S. Dak.	[.07+.26+.61+.01+.00]	"	[.00+.11+.00]	=		.84		.85
	Upton, Wyo.	[.09+.05+.76+.01+.00]	"	[.00+.07+.00]	=		.84		.86



ture of the materials it was not feasible to determine the soluble salts in these samples on a water extract; consequently the exact cations belonging to the soluble anions are not known.

Of the 10 samples that were identical with those listed by Ross and Hendricks, the value obtained for cation-exchange capacity in the present study agreed with that given by them for only three, Nos. 3, 13, and 20. For the other seven samples higher values, ranging from 0.17 to 0.31 milliequivalents per gram, were obtained. The values given by them for observed cation exchange ranged between 0.66 and 1.00 milliequivalents per gram, the mean value being 0.84. In the present study the values, for all the samples examined, ranged between 0.80 and 1.15, with a mean value of 0.95. This discrepancy may be due to the different procedures used in the two studies for the determination of cation-exchange capacity.

Of particular interest is the fact that magnesium was found in the cation-exchange filtrate of all the samples. In several of the samples, Nos. 12, 14, and that from Upton, Wyo., the soluble anions were more than equivalent to the magnesium found; and there is the possibility that in these samples the magnesium found in the cation-exchange filtrate was present in the sample as carbonate, sulfate, and/or chloride. In all the other samples, however, there seems to be little doubt that magnesium is present as an exchangeable cation. In three samples, Nos. 22, 24, and that from Pala, Calif., it is the dominant exchange cation and amounts to 24.5, 32.0, and 28.8 per cent, respectively, of the total magnesium in the samples. Two of these samples, Nos. 22 and 24, were ones whose sum of the milliequivalents per gram of Ca, Na, and K, in Ross and Hendricks' table, was much lower than the observed cation-exchange capacity. In the Fort Steel, Wyo., sample the exchangeable magnesium is almost equivalent to exchangeable calcium, the dominant cation, and amounts to 14.6 per cent of the total magnesium in the sample. These results indicate that the presence of exchangeable magnesium in the montmorillonite clays is more common than is generally recognized and that it may constitute an important proportion of the total magnesium in the clay.

The close agreement between the sum of the milliequivalents of exchanged cations—treating calcium and magnesium entirely as divalent cations—with the determined cation-exchange capacity suggests that these cations are actually present as divalent cations and that no significant portion of them is present as univalent basic cations as postulated by Bower and Truog.<sup>5</sup> These investigators found that the cation-exchange

<sup>5</sup> Bower, C. A., and Truog, F., Base-exchange capacity as influenced by the nature of the cation employed and basic salts: *Soil. Sci. Soc. Am. Proc.*, 5, 86-89 (1940).

capacity of a bentonite is significantly higher when determined with divalent cations than when determined with univalent cations; they attributed the higher values obtained with divalent cations to the formation of a basic salt with the weak clay acid to a varying degree, depending on the strength of the base which the cation in question forms. According to their results, cation-exchange is 7 and 12 per cent higher, respectively, when determined with calcium and magnesium acetate than when determined with sodium, potassium, or ammonium acetate. If basic cations of calcium and magnesium form such significant proportions of the exchange cations of a natural calcium or magnesium montmorillonite, failure to consider this in the summation of the milliequivalents of the exchange cations would result in a considerable discrepancy between such a summation and the cation-exchange capacity as determined with a univalent cation, particularly for such samples as those from Santa Rosa, Mexico (No. 24), and from Pala, Calif., in which magnesium is the dominant exchangeable cation.

#### EFFECT OF EXCHANGEABLE MAGNESIUM AND OBSERVED CATION-EXCHANGE CAPACITY ON THE CALCULATED FORMULA

Formulas for the samples used in the cation-exchange studies, calculated according to the method of Ross and Hendricks, are given in Table 2. On the left side of the table appears the formula obtained when all the magnesium is assigned to the octahedral group and when 0.33, the average value for cation-exchange capacity obtained by Ross and Hendricks, was used. On the right side of the table appears the formula obtained when the value used for magnesium in octahedral coordination was obtained by subtracting the amount of magnesium found in the cation-exchange filtrate from the total magnesium content of the sample and when the determined value for cation-exchange, not an average value, was used in the calculation.



In suggesting  $[\text{Al}_{1.67}\text{Mg}_{.33}]\text{Si}_4\text{O}_{10}[\text{OH}]_2$  as the most suitable generalized formula for montmorillonite, Ross and Hendricks stated that "the only serious flaw in it is that the total number of ions in octahedral coordination is 2.00, whereas in all actual specimens this number is exceeded. In the formulas obtained by them, the number of ions in octahedral coordination ranged from 2.02 to 2.27, with the number of ions in octahedral coordination being apparently somewhat higher toward the beidelite end. This increase in the number of ions in octahedral coordination was interpreted as evidence of a tendency toward internal compensation of charge as the amount of aluminum in tetrahedral coordination is increased.

TABLE 2. FORMULAS FOR MONTMORILLONITE CLAYS

No.	Locality	Mg all in lattice—mean cation-exchange	Non-exchangeable Mg in lattice—observed cation-exchange
3	Amargosa, Valley, Calif.	$\frac{2.08}{[Al_{1.40}^{+3}Fe_{1.14}^{+3}Fe_{0.1}^{+2}Mg_{.38}] [Si_{3.88}Al_{.02}^{+4}O_{10}(OH)_2]_{x.33}}$	$\frac{2.02}{[Al_{1.37}^{+3}Fe_{1.14}^{+3}Fe_{0.1}^{+2}Mg_{.60}] [Si_{3.97}Al_{.03}^{+4}O_{10}(OH)_2]_{x.48}}$
6	Tatatila, Mexico	$\frac{2.05}{[Al_{1.68}^{+3}Mg_{.42}] [Si_{1.94}Al_{.06}^{+3}O_{10}(OH)_2]_{x.33}}$	$\frac{2.01}{[Al_{1.61}^{+3}Mg_{.40}] [Si_{1.92}Al_{.08}^{+3}O_{10}(OH)_2]_{x.45}}$
10	Nieder-Bayern, Germany	$\frac{2.05}{[Al_{1.44}^{+3}Fe_{.21}Mg_{.40}] [Si_{1.94}Al_{.06}^{+3}O_{10}(OH)_2]_{x.33}}$	$\frac{2.02}{[Al_{1.46}^{+3}Fe_{.21}Mg_{.38}] [Si_{1.94}Al_{.07}^{+3}O_{10}(OH)_2]_{x.36}}$
12	Ardmore, S. Dak.	$\frac{2.05}{[Al_{1.48}^{+3}Fe_{.15}Fe_{.02}Mg_{.40}] [Si_{1.92}Al_{.08}^{+3}O_{10}(OH)_2]_{x.33}}$	$\frac{2.02}{[Al_{1.47}^{+3}Fe_{.15}Fe_{.02}Mg_{.38}] [Si_{1.91}Al_{.09}^{+3}O_{10}(OH)_2]_{x.43}}$
13	Irish Creek, Va.	$\frac{2.06}{[Al_{1.50}^{+3}Fe_{.14}Mg_{.42}] [Si_{1.91}Al_{.09}^{+3}O_{10}(OH)_2]_{x.33}}$	$\frac{2.01}{[Al_{1.48}^{+3}Fe_{.14}Mg_{.39}] [Si_{1.91}Al_{.09}^{+3}O_{10}(OH)_2]_{x.45}}$
14	Hector, Calif.	$\frac{2.07}{[Al_{1.49}^{+3}Fe_{.13}Fe_{.01}Mg_{.44}] [Si_{1.90}Al_{.10}^{+3}O_{10}(OH)_2]_{x.33}}$	$\frac{2.02}{[Al_{1.46}^{+3}Fe_{.12}Fe_{.01}Mg_{.42}] [Si_{1.87}Al_{.13}^{+3}O_{10}(OH)_2]_{x.50}}$
20	Lemon, Miss.	$\frac{2.12}{[Al_{1.43}^{+3}Fe_{.16}Fe_{.01}Mg_{.52}] [Si_{1.84}Al_{.13}^{+3}O_{10}(OH)_2]_{x.33}}$	$\frac{2.06}{[Al_{1.46}^{+3}Fe_{.13}Fe_{.01}Mg_{.44}] [Si_{1.88}Al_{.11}^{+3}O_{10}(OH)_2]_{x.39}}$
22	Atzacapozcalco, Mexico	$\frac{2.08}{[Al_{1.34}^{+3}Fe_{.30}Mg_{.44}] [Si_{1.87}Al_{.13}^{+3}O_{10}(OH)_2]_{x.33}}$	$\frac{2.02}{[Al_{1.37}^{+3}Fe_{.31}Mg_{.34}] [Si_{1.89}Al_{.11}^{+3}O_{10}(OH)_2]_{x.41}}$
24	Santa Rosa, Mexico	$\frac{2.13}{[Al_{1.56}^{+3}Mg_{.57}] [Si_{1.88}Al_{.15}^{+3}O_{10}(OH)_2]_{x.33}}$	$\frac{2.01}{[Al_{1.62}^{+3}Mg_{.39}] [Si_{1.89}Al_{.11}^{+3}O_{10}(OH)_2]_{x.44}}$
28	Greenwood, Maine	$\frac{2.05}{[Al_{1.74}^{+3}Fe_{.01}Mg_{.30}] [Si_{1.83}Al_{.17}^{+3}O_{10}(OH)_2]_{x.33}}$	$\frac{2.01}{[Al_{1.71}^{+3}Fe_{.01}Mg_{.29}] [Si_{1.81}Al_{.19}^{+3}O_{10}(OH)_2]_{x.45}}$
	Fort Steel, Wyo.	$\frac{2.03}{[Al_{1.51}^{+3}Fe_{.13}Mg_{.39}] [Si_{1.97}Al_{.03}^{+3}O_{10}(OH)_2]_{x.33}}$	$\frac{2.00}{[Al_{1.53}^{+3}Fe_{.13}Mg_{.34}] [Si_{1.98}Al_{.02}^{+3}O_{10}(OH)_2]_{x.36}}$
	Pala, Calif.	$\frac{2.12}{[Al_{1.66}^{+3}Fe_{.01}Mg_{.45}] [Si_{1.78}Al_{.22}^{+3}O_{10}(OH)_2]_{x.33}}$	$\frac{2.02}{[Al_{1.67}^{+3}Fe_{.01}Mg_{.32}] [Si_{1.81}Al_{.19}^{+3}O_{10}(OH)_2]_{x.42}}$
	Belle Fourche, S. Dak.	$\frac{2.03}{[Al_{1.55}^{+3}Fe_{.18}Fe_{.02}Mg_{.28}] [Si_{1.89}Al_{.11}^{+3}O_{10}(OH)_2]_{x.33}}$	$\frac{2.00}{[Al_{1.57}^{+3}Fe_{.13}Fe_{.02}Mg_{.22}] [Si_{1.91}Al_{.09}^{+3}O_{10}(OH)_2]_{x.45}}$
	Upton, Wyo.	$\frac{2.03}{[Al_{1.55}^{+3}Fe_{.17}Fe_{.03}Mg_{.25}] [Si_{1.94}Al_{.06}^{+3}O_{10}(OH)_2]_{x.33}}$	$\frac{2.00}{[Al_{1.56}^{+3}Fe_{.17}Fe_{.03}Mg_{.24}] [Si_{1.93}Al_{.07}^{+3}O_{10}(OH)_2]_{x.40}}$

The value of 0.33 for the exchange cations in the generalized formula for montmorillonite was used because 26 of their 54 samples had a total equivalence of  $\text{Na} + \text{Ca}/2 + \text{K}$  approximately equal to 0.33, which was in agreement with the mean value of 0.84 milliequivalents for cation-exchange capacity found by Ross and Hendricks.

In the formulas shown in Table 2 of the samples used in this study, the number of ions in octahedral coordination ranges from 2.01 to 2.13 when all the magnesium is assigned to the octahedral group and when an average cation-exchange value of 0.33 is used. When, however, only non-exchangeable magnesium is assigned to the octahedral group and when the determined cation-exchange value is used, the number of ions in octahedral coordination for the same samples is very close to the theoretical 2.00, ranging from 1.99 to 2.03 except for one sample, No. 20, for which the number of ions was 2.06 as compared with 2.12 by the first method of calculation.

Correction of total magnesium for exchangeable magnesium and use of the determined cation-exchange value in calculating the formula has little effect on the number of ions in octahedral coordination if the exchangeable magnesium is small and if the cation-exchange capacity is near the average value of 0.33 used by Ross and Hendricks. For example, the sample from Upton, Wyo., had only 0.10 per cent exchangeable magnesium and a cation-exchange capacity of 0.86 milliequivalents per gram as compared with the mean value of 0.84 found by Ross and Hendricks. The number of ions in octahedral coordination is 2.03 when all the magnesium is calculated as in octahedral coordination and 0.33 is used as the cation-exchange value and 2.00 when total magnesium is corrected for exchangeable magnesium and the determined cation-exchange value is used. However, if a sample has high exchangeable magnesium and/or high cation-exchange capacity, correction of total magnesium for exchangeable magnesium and use of the determined cation-exchange value in calculating the formula has considerable effect on the number of ions found to be in octahedral coordination. The highest exchangeable magnesium was found in sample No. 24, in which it amounted to 1.62 per cent, approximately one-third of the total magnesium content of the sample. The cation-exchange capacity is also fairly high, being 0.98 milliequivalents per gram. When all the magnesium of this sample is calculated as in the octahedral group and an exchange value of 0.33 is used, the number of ions in octahedral coordination is 2.13 as compared with 2.01 ions in octahedral coordination when only non-exchangeable magnesium is calculated as in the octahedral group and the determined cation-exchange value is used. The number of positions occupied in the octahedral group by Mg fell from 0.57 to 0.39 and Al in

tetrahedral coordination fell from 0.15 to 0.11. Sample No. 14 has very little exchangeable magnesium, only 0.11 per cent, but very high cation-exchange capacity, 1.15 milliequivalents per gram. Correcting for exchangeable magnesium in this sample has no effect on the number of ions in octahedral coordination, but use of the determined cation-exchange value instead of 0.33 lowers the number of ions in octahedral coordination from 2.07 to 2.02, and raises the Al in tetrahedral coordination from 0.10 to 0.13. It is apparent, therefore, that correction of total magnesium for exchangeable magnesium and the use of the determined cation-exchange value is of considerable importance in calculating the formulas of the montmorillonites; of as much importance as any of the other analytical values. When these modifications are made in calculating the formula, the number of ions found to be in octahedral coordination is very close to the theoretical value of 2.00. This suggests that substitution of Mg for Al in the octahedral group is ion for ion, and that there is little or no tendency toward internal compensation of charge by the filling of extra positions.

#### INFORMATION FURNISHED BY MARSHALL'S METHOD OF CALCULATION

A comparison of the number of atoms in the octahedral layer of the unit cell by Marshall's method<sup>6</sup> of calculation when (1) all the magnesium is assigned to the octahedral layer, and (2) when only non-exchangeable magnesium is assigned to this layer is shown in Table 3.

In recalculating the analysis for sample No. 24, the number of atoms in the octahedral layer is 4.400 when all the magnesium is assigned to this layer, and 4.032 when only non-exchangeable magnesium is assigned to the same layer. The 0.400 in excess of 4.00 found in the first calculation is equivalent to 1.78 per cent of MgO, as compared with 1.62 per cent of exchangeable magnesium as MgO found on determination. When all the magnesium is assigned to the octahedral layer that layer appears to carry a plus charge of 0.060, the total charge on the cell amounts to only  $-0.156$ , and the charge due to the cations—CaO, Na<sub>2</sub>O, and K<sub>2</sub>O—is only  $-0.154$ . But when only non-exchangeable magnesium is assigned to the octahedral layer, that layer has a negative charge of 0.668, the total charge on the cell is 0.884, and the charge due to the exchangeable cations is 0.881. Determined cation-exchange capacity was 0.886. For the sample from Fort Steel, Wyo., there are 4.113 atoms in the octahedral layer when all the magnesium is assigned to that layer as compared to 3.990 atoms when correction is made for exchangeable magnesium and

<sup>6</sup> Marshall, C. E., The colloid chemistry of the silicate minerals: *Am. Soc. Agron. Monograph Ser.*, 1, p. 58, Academic Press, Inc., New York, N. Y. (1949).



the charge on this layer rises from 0.458 to 0.704. The total charge on the unit cell is only  $-0.482$  when all the magnesium is assigned to the octahedral layer and is  $-0.728$  when only non-exchangeable magnesium is assigned to that layer. The charge due to the exchangeable cations is 0.729 as compared with a determined cation-exchange capacity of 0.718. The excess atoms found in the octahedral layer when all the magnesium is assigned to that layer are equivalent to 0.49 per cent MgO. Exchangeable MgO in the cation-exchange filtrate was 0.52 per cent. Thus when the formula is calculated from the analysis by Marshall's method and all magnesium assigned to the octahedral layer, it is possible to estimate, from the excess atoms over 4.00 in the octahedral layer, the amount of exchangeable magnesium present in the sample to within a few tenths of a per cent. It is also possible to estimate the cation-exchange capacity of the sample by subtracting the excess atoms over 4.00 from the number of atoms of MgO before calculating the charge on the octahedral layer. For example, if 0.400 is subtracted from 1.140 (the number of atoms of magnesium in the octahedral layer when all the magnesium is assigned to that layer) and the remainder (0.740) used in calculating the charge on that layer, a total charge for the unit cell, or the cation-exchange capacity, for sample No. 24 of 0.956 is obtained, whereas the determined cation-exchange capacity of this sample was 0.890. If the same calculation is made for the sample from Fort Steel, Wyo., an estimated cation-exchange capacity of 0.708 is obtained, compared to a determined cation-exchange capacity of 0.718. When exchangeable magnesium is low, assignment of all magnesium to the octahedral layer involves no considerable error, although even in such a sample the number of atoms obtained in the octahedral layer is somewhat high and the charge on the unit cell is proportionately low. Sample No. 14 had only 0.11 per cent exchangeable magnesium on determination. If this is assigned with non-exchangeable magnesium to the octahedral layer, the number of atoms obtained in this layer on calculation is 4.066 and the charge on the unit cell is 0.953 as compared with 4.040 atoms in the octahedral layer and a charge of 1.009 on the unit cell when total magnesium is corrected for exchangeable magnesium. The determined cation-exchange of this sample was 1.000. If the excess atoms above 4.000 obtained in the octahedral layer when all the magnesium is assigned to that layer are converted to their equivalent in terms of MgO, they indicate an exchangeable MgO of 0.31 per cent—0.20 per cent higher than the exchangeable MgO found on determination but indicative of the degree of magnitude of the exchangeable magnesium and within the limits of the analytical error involved when all the analytical values used in the calculation are taken into consideration.

TABLE 3. COMPARISON OF NUMBER OF ATOMS IN THE OCTAHEDRAL LAYER OF THE UNIT CELL WHEN (1) ALL Mg IS ASSIGNED TO OCTAHEDRAL LAYER AND (2) ONLY NON-EXCHANGEABLE Mg IS ASSIGNED TO OCTAHEDRAL LAYER

All Mg assigned to octahedral layer						Only non-exchangeable Mg assigned to octahedral layer					
Percentage composition	G-equiv. of cationic constits.	G-equiv. per total of 44	Atoms per unit cell	Charge		Percentage composition	G-equiv. of cationic constits.	G-equiv. per total of 44	Atoms per unit cell	Charge	
Sample No. 24—Santa Rosa, Mexico											
SiO <sub>2</sub>	51.50	3.430	31.143	7.786	7.786 { .214 } — .214	SiO <sub>2</sub>	51.50	3.430	31.143	7.786	7.786 { .214 } — .214
					8.000						8.000
Al <sub>2</sub> O <sub>3</sub>	19.44	1.144	10.387	3.462	— 3.248	Al <sub>2</sub> O <sub>3</sub>	19.44	1.144	10.387	3.462	— 3.248
Fe <sub>2</sub> O <sub>3</sub>	.10	.004	.036	.012	+ .060	Fe <sub>2</sub> O <sub>3</sub>	.10	.004	.036	.012	— .068
MgO	5.07	.251	2.279	1.140	1.140	MgO	3.45	.171	1.553	.776	.776
					4.400 — .154						4.036 — .884
CaO	.40	.014	.127	.127	.127	CaO	.40	.014	.127	.127	.127
Na <sub>2</sub> O	.06	.002	.018	.018	.018	MgO	1.62	.080	.727	.727	.727
K <sub>2</sub> O	.04	.001	.009	.009	.009	Na <sub>2</sub> O	.06	.002	.018	.018	.018
					E = .154	K <sub>2</sub> O	.04	.001	.009	.009	.009
										E = .881	.881
Excess atoms in octahedral layer equiv. to 1.78 per cent MgO											
						Detd. cation-exchange					
Fort Steel, Wyo.	53.37	3.554	31.903	7.976	7.976 { .024 } — .024	SiO <sub>2</sub>	53.37	3.554	31.903	7.976	7.976 { .024 } — .024
					8.000						8.000
Al <sub>2</sub> O <sub>3</sub>	17.53	1.032	9.261	3.087	— 3.063	Al <sub>2</sub> O <sub>3</sub>	17.53	1.032	9.261	3.087	— 3.063
Fe <sub>2</sub> O <sub>3</sub>	2.25	.084	.758	.253	— .472	Fe <sub>2</sub> O <sub>3</sub>	2.25	.085	.758	.253	— .704
MgO	3.58	.176	1.580	.790	.790	MgO	3.03	.150	.674	.674	.674
					4.106 — .496						.990 — .728

All Mg assigned to octahedral layer				Only non-exchangeable Mg assigned to octahedral layer			
Percentage Composition	G-equiv. of cationic constituents, of 44	Atoms per unit cell	Charge	Percentage composition	G-equiv. of cationic constituents, of 44	Atoms per unit cell	Charge
CaO	.84	.269	.269	CaO	.84	.269	.269
Na <sub>2</sub> O	.00	.000	.000	MgO	.52	.232	.232
K <sub>2</sub> O	.02	.004	.004	Na <sub>2</sub> O	.00	.000	.000
H	.025	.224	.224	K <sub>2</sub> O	.02	.004	.004
	<u>4.901</u>		<u>E = .497</u>	H	.025	.224	.224
					<u>4.901</u>		<u>E = .729</u>
Excess atoms in octahedral layer equivalent to 0.48 per cent MgO				Detd. cation-exchange			
					.080		.718
Sample No. 14—Hector, Calif.							
SiO <sub>2</sub>	53.02	3.532	30.945	SiO <sub>2</sub>	53.02	3.532	30.945
		7.736	7.736			7.736	7.736
		.264	.264			.264	.264
			<u>8.000</u>				<u>8.000</u>
Al <sub>2</sub> O <sub>3</sub>	18.50	1.089	9.543	Al <sub>2</sub> O <sub>3</sub>	18.50	1.089	9.543
Fe <sub>2</sub> O <sub>3</sub>	2.33	.088	.771	Fe <sub>2</sub> O <sub>3</sub>	2.33	.088	.771
FeO	.13	.004	.035	FeO	.13	.004	.035
MgO	4.04	.200	1.753	MgO	3.93	.194	1.700
			<u>4.067</u>				<u>4.041</u>
			<u>E = .956</u>				<u>1.008</u>
CaO	.32	.096	.096	CaO	.32	.096	.096
Na <sub>2</sub> O	3.28	.106	.929	MgO	.11	.006	.052
K <sub>2</sub> O	.08	.002	.017	Na <sub>2</sub> O	3.28	.106	.929
			<u>1.042</u>	K <sub>2</sub> O	.08	.002	.017
			<u>E = .954</u>				<u>1.094</u>
							<u>.088</u>
Soluble anions	5.032	.010		Soluble anions			
	<u>5.022</u>				<u>5.021</u>		<u>E = 1.006</u>
Excess atoms in octahedral layer equivalent to 0.31 per cent MgO				Detd. cation-exchange			
							1.150
							1.008

Thus, by the Marshall method, the number of atoms obtained in the octahedral layer in excess of 4.00, when all magnesium is assigned to the octahedral layer, permits an estimation of the amount of exchangeable magnesium present and of the cation-exchange capacity of the sample. On the other hand, when exchangeable magnesium is determined and only non-exchangeable magnesium is assigned to the octahedral layer, the number of atoms in this layer is very close to the theoretical 4.00, even when exchangeable magnesium is high (as in sample No. 24) and the charge on the unit cell checks the charge of the external cations and the determined cation-exchange capacity, provided, of course, that correction has been made for soluble salts that may be present.

#### ACKNOWLEDGMENTS

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# A METHOD FOR THE PREPARATION OF POLISHED THIN SECTIONS OF MINERAL GRAINS

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## ABSTRACT

This paper describes a method of preparing polished thin sections of crushed mineral grains for microscopic examination. Polished thin sections permit the examination of a section of each grain in both reflected light and transmitted light. The technique described is applicable to the study of ores containing intimate associations of transparent minerals with semiopaque or opaque minerals.

During work on the concentration of a Bolivian tin ore at Battelle Memorial Institute in 1948, a method was developed for the preparation of polished thin sections of mineral grains. The purpose of this method was to permit the examination of a section of each grain both by vertically reflected light and by polarized transmitted light.

In the study of this ore, the standard methods of microscopic examination were not adequate. Examination of polished briquettes was of limited value because several of the minerals appeared similar in reflected light and, therefore, could not always be identified by this method alone. Petrographic examination of grains in refractive index media was also unsatisfactory because the intimate association of minerals caused most of the grains to be nearly opaque. However, by the use of polished thin sections, which combined most of the advantages of polished briquettes and thin sections, it was possible to identify the different minerals in each mineral aggregate. This method permitted a statistical study of the ground ore and the products of concentration to determine the degree of association of the valuable mineral (cassiterite) with each of the gangue minerals.

Several articles have been published on the preparation of polished thin sections of individual pieces of rock. The most recent of these are the papers by Kennedy (1) and Meyer (2). A method for preparing thin sections of crushed grains is described by Gibbs and Evans (3). However, to the author's knowledge, no literature exists on the preparation of *polished* thin sections of crushed *grains*.

Because it is considered probable that the use of polished thin sections of grains will be helpful in concentration studies on complex ores, the method used to prepare the specimens is described herein.

## GENERAL PROCEDURE

Briefly, the procedure in preparing the specimens is as follows: A single layer of sized grains is mounted in a film of plastic on a flat surface of the same plastic. The layer is ground to nearly the center of the grains,



and this ground surface is remounted on more of the same plastic. The original piece of plastic is then cut off and the other side of the layer of grains is ground until the section is of the desired thickness. The surface is then polished.

The completed specimens can best be examined by means of a polarizing petrographic microscope equipped with a vertical illuminator. An electrical switch for changing from reflected light to transmitted light, and vice versa, while observing a grain through the microscope, facilitates the examination.

### MOUNTING MEDIUM

The resin selected for mounting the mineral grains was diallyl phthalate prepolymer,\* a solution of the polymer in the monomer. It is a thermosetting resin which, unlike Lucite and Bakelite, cannot be melted after polymerizing. Thus it can readily be sawed, ground, and polished without the difficulty caused by softening encountered in the use of Lucite. The color is light amber, but a section 1/10 inch thick appears practically colorless under the microscope. One of the reasons for selecting diallyl phthalate was that its refractive index, 1.57, is between the indices of quartz and tourmaline, the major gangue minerals in the ore.

Because of the shrinkage on polymerizing, slow curing is necessary to minimize strains in the plastic. If the curing is too rapid, the strain birefringence in the plastic interferes with determination of birefringence in the mineral grains.

### PREPARATION OF SPECIMENS

The grains to be mounted should be reasonably well sized; the fractions obtained from the standard Tyler  $\sqrt{2}$  screen series are suitable. The mounting of grains within the size range from 10 to 150 mesh falls into seven steps. For grains finer than 150 mesh and for elutriation products, some of the steps are omitted. These are discussed under Special Cases. Details of grinding and polishing techniques and equipment used are omitted because of the variation in equipment in different laboratories and because no special grinding and polishing equipment is required other than that used for preparing ordinary thin sections and polished sections.

#### *Step 1—Preparation of Liquid Plastic*

Prepare a quantity of the plastic by adding 1 gram of catalyst, tertiary

\* Diallyl phthalate prepolymer is produced by the Shell Chemical Corporation, 500 Fifth Avenue, New York 18, N. Y.

butyl perbenzoate,† to each 100 grams of diallyl phthalate prepolymer. Stir well and store in a closed bottle. This prepared solution will keep for several months at room temperature without becoming noticeably more viscous.

#### *Step 2—Preparation of Blanks*

Prepare a number of blanks as follows. Apply silicone stop-cock grease to the inside surface of a glass vial or test tube with an inside diameter of one inch. Fill with diallyl phthalate and cure for 24 hours at 80° C, 24 hours at 90° C, 24 hours at 100° C, and 24 hours, or until hard, at 110° C. (The long curing cycle in this step is necessary because of the large size of the casting. If cured more rapidly, the plastic may crack in several places.) Allow to cool and then shake the plastic loose from the tube. Saw the plastic cylinder into discs about  $\frac{1}{2}$  inch thick. A large number of these blanks may be prepared at one time and stored for future use.

#### *Step 3—Mounting Grains on Blanks*

To mount a single layer of grains on a blank, proceed as follows. Grind one surface of the blank to make it smooth enough that the depth of the remaining scratches is less than one-tenth the diameter of the grains which are to be mounted. Wash the smooth surface of the blank with alcohol. Place 2 to 6 drops of diallyl phthalate on the blank, depending on the size of grains, and spread it over the surface. Add enough of the mineral grains to form not more than one layer and distribute them evenly over the surface by means of a piece of fine wire. Add more diallyl phthalate if necessary to completely cover all the grains. (Surface tension will keep the liquid from running over the edge of the blank.) Place on a level surface in an oven and cure for 48 hours at 110° C.

#### *Step 4—Grinding to Near Center of Layer of Grains*

Grind the specimen, starting with coarse abrasive and finishing with fine, until ground nearly to the center of the layer of grains. This step requires practice to prevent grinding out some of the grains. For the final grinding, any method which has been found satisfactory for ordinary thin sections may be used.

#### *Step 5—Remounting the Ground Surface*

To remount the ground surface, form a cup  $\frac{1}{2}$  inch high above the layer of grains by wrapping Scotch cellophane tape around the specimen.

† Obtainable from the Union Bay State Co., Cambridge, Mass.

Fill the cup with diallyl phthalate and cure at 110° C for 48 hours or until the plastic is hard.

*Step 6—Grinding and Polishing Opposite Side of Grains*

To provide a means for measuring the thickness of the sections, grind four sides of the cylinder perpendicular to the layer of grains until a few grains are exposed on each side. Then saw off most of the original blank. Grind the layer of grains starting with coarse abrasive and finish-

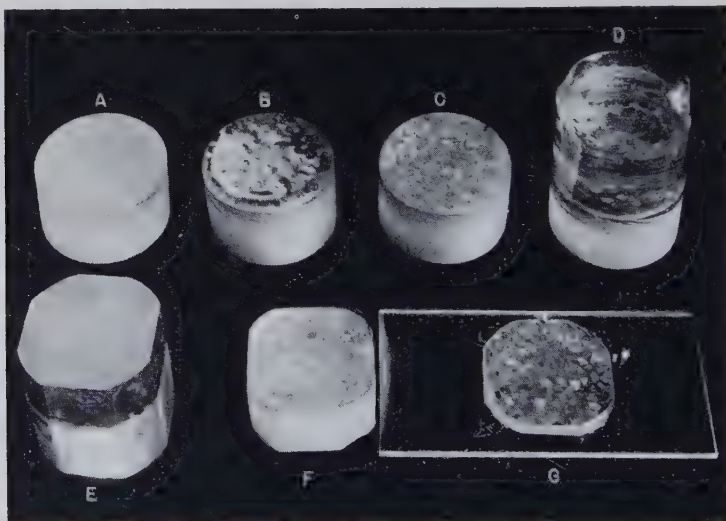


FIG. 1. Stages in Preparation of a Polished Thin Section of Mineral Grains.

- (a) Blank ready for mounting grains.
- (b) Layer of grains mounted in plastic on surface of blank.
- (c) Specimen ground to near center of layer of grains.
- (d) Ground surface remounted on plastic. Wavy surface of Scotch tape is due to shrinkage of plastic on curing.
- (e) Four sides ground on specimen to provide a means for measuring thickness of section.
- (f) Opposite side of layer of grains ground and polished. Note that (f) represents top half of (e) inverted.
- (g) Plastic reduced in thickness and mounted on glass slide.

ing with fine until the section is the desired thickness. During the grinding, the thickness of the grains on all four edges of the specimen should be checked at intervals by observing through the petrographic microscope with a micrometer ocular.

The specimen may now be polished by any method which is suitable for ordinary polished briquettes of the same minerals, provided it does not remove too much of the thickness of the section.

*Step 7—Reducing Thickness of Plastic and Mounting on Glass Slide*

For some purposes, the specimen may be considered completed at the end of Step 6. However, if the color or birefringence of the plastic is objectionable, the thickness of the plastic mount can readily be reduced to about 1/10 inch by grinding. If desired, the specimen can be mounted on a glass slide with a few small drops of Duco cement around the edge.

*Special Cases*

In the case of sized grains finer than 150 mesh, it is not necessary to grind both sides of the layer of grains, as the sections are sufficiently thin after grinding to the center of the layer. Therefore, the specimens can be polished after Step 4 and completed as in Step 7.

In the case of elutriated products, where there is a difference in size between minerals of different specific gravities, the following variation is suggested. Omit Steps 2 and 3. Mix one or two grams of the grains in a vial with sufficient diallyl phthalate to cover, and cure at the same temperatures as used in Step 2. With a diamond saw, cut the cylinder perpendicular to the axis into two equal parts. Grind the cut surface of one of the halves, and complete the specimen as in Steps 5, 6, and 7.

## ACKNOWLEDGMENT

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# FERROCARPHOLITE, THE HITHERTO UNKNOWN FERROUS IRON ANALOGUE OF CARPHOLITE PROPER

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## ABSTRACT

Ferrocapholite, the hitherto unknown ferrous iron analogue of carpholite proper, was found as a magnesian variety with the formula  $H_4(Fe, Mg)Al_2Si_2O_{10}$ . It builds dark green prismatic crystals in a cobble of vein-quartz collected West of Tomata, eastern Central Celebes, by the late Dr. Ir. W. H. Hetzel (Celebes expedition of 1929 of the Netherlands Indies Geological Survey under the leadership of Prof. Dr. H. A. Brouwer). It is orthorhombic dipyramidal with  $a_0=13.77 \text{ \AA}$ ,  $b_0=20.18 \text{ \AA}$ ,  $c_0=5.11 \text{ \AA}$ ;  $a_0:b_0:c_0=0.682:1:0.253$ , and the space-group is *Ccca*. The unit-cell contains  $8H_4(Fe, Mg)Al_2Si_2O_{10}$ . Observed crystal faces:  $\{010\}$ ,  $\{100\}$  and  $\{110\}$ ; cleavage  $\{010\}$  perfect,  $\{110\}$  indistinct. Twinning was not observed. Hardness  $5\frac{1}{2}$ ; fusibility  $3\frac{1}{2}$ ; sp. gr. 3.04;  $\gamma=1.647$ ,  $\beta=1.644$ ,  $\alpha=1.628$ ,  $2V_\alpha=49^\circ$ , dispersion weak  $r>v$ , with reference to  $\alpha$ ;  $c=\gamma$ ,  $b=\alpha$ ,  $a=\beta$ . Pleochroism in thin section varies from yellow-green ( $\alpha$  and  $\beta$ ) to very light blue-green ( $\gamma$ ). The optical characteristics of ferrocapholite correspond almost entirely to those of carpholite proper,  $H_4MnAl_2Si_2O_{10}$ .

Comparable practically manganese-free carpholite-like material, probably magnesian ferrocapholite with a larger content of magnesium, was found in situ at two other localities in eastern Central Celebes.

## INTRODUCTION

During the latter part of the last world war the author studied a collection of igneous and metamorphic rocks from eastern Central Celebes, collected by the 1929 expedition of the Netherlands Indies Geological Survey under the leadership of Prof. Dr. H. A. Brouwer. Four of the investigated samples were found to contain minerals with the optical characteristics of carpholite,  $H_4MnAl_2Si_2O_{10}$ . One of these, a blastopsammitic schistose carpholite-quartzite, appeared on qualitative chemical investigation to show a considerable content of manganese, which checked the optical determination as carpholite. The content of manganese of the carpholite-like material in the three other samples, however, appeared to be negligible in comparison to that of carpholite from Wippra, one of the main localities of this comparatively rare mineral. One of these three samples (No. 15-161<sup>x</sup>) was found to contain a large quantity of the carpholite-like material; this sample, which consists of vein-quartz with the said mineral, was found by the late Dr. Ir. W. H. Hetzel as a cobble west of Tomata.<sup>1</sup> In the two other samples the mineral is of subordinate or local occurrence. More detailed chemical investigations

<sup>1</sup> For the exact position of the locality mentioned the reader is referred to the author's paper on the igneous and metamorphic rocks from eastern Central Celebes, page 72.



were performed on the material from the vicinity of Tomata. Since it was not possible to have quantitative chemical analyses made during the latter part of the war, only the results of a spectrochemical analysis by Dr. R. Schmidt could be given in the author's paper on the rocks from eastern Central Celebes. According to this analysis by Dr. Schmidt the mineral from the vicinity of Tomata contained mainly magnesium, iron, aluminum and silicon; the concentration of magnesium was estimated to be at least twenty times as large as the concentration of manganese. Since Jakob and Hesemann (1927) had described a magnesian carpholite with predominant manganese from Hettstedt (Harz), which could be optically distinguished only with difficulty from the more manganese-rich varieties of this mineral, the material from Celebes was first thought to represent the still unknown magnesium analogue of carpholite proper; the material, however, remained unnamed pending a quantitative chemical analysis.

According to a second spectrochemical analysis by Dr. Schmidt, the results of which were not included in the paper on the rocks from eastern Central Celebes, the content of iron appeared to be much larger than that of magnesium. This was confirmed by a quantitative chemical analysis performed in the year 1949. The material from the vicinity of Tomata, therefore, appeared to represent the hitherto unknown ferrous iron analogue of carpholite proper, for which the name *ferrocarpholite* is proposed. Besides the optic data already published in 1947, this paper contains mainly new chemical and x-ray data.

The author is indebted to Prof. Dr. H. A. Brouwer for affording him the opportunity to study this interesting mineral.

#### CHEMICAL PROPERTIES

A quantitative chemical analysis was performed on material from the sample that was found west of Tomata (No. 15-161<sup>x</sup>). Quartz and heavy minerals from some parts of the sample, in which no ore was observed, were separated with the aid of bromoform. During the drying process, which was not performed by the author himself, a small amount of water may have been lost. After further purifying by means of a magnetic treatment and hand-picking, the concentrate appeared to be practically pure.

The average of duplicate analyses of this material is given in Table 1, together with the deviations of the separate analyses. For some of the minor constituents no duplicate data are available owing to lack of material. For  $H_2O+$  a lower percentage was obtained during the first determination; the percentage given in Table 1 was obtained after prolonged heating at the request of the author. The difficulties encoun-

TABLE 1. CHEMICAL ANALYSIS, RATIOS, AND EMPIRICAL UNIT-CELL CONTENTS OF FERROCAPHOLITE

	1	2	3		4	
SiO <sub>2</sub>	37.38 ( $\pm 0.04$ )	37.59	0.6259	Si	16.27	8 $\times$ 2.03
Al <sub>2</sub> O <sub>3</sub>	29.23 ( $\pm 0.01$ )	29.39	0.2883	Al	14.99	
Fe <sub>2</sub> O <sub>3</sub>	2.06 ( $\pm 0.02^b$ )	2.07	0.0130	Fe'''	0.68	15.81
TiO <sub>2</sub>	0.22 ( $\pm 0.00^b$ )	0.22	0.0028	Ti	0.07	
MgO	2.51 ( $\pm 0.05^b$ )	2.52	0.0625	Mg	1.63 { 0.07	
MnO	0.14 ( $\pm 0.00^b$ )	0.14	0.0020		1.56	
FeO	17.88 ( $\pm 0.01^b$ )	17.98	0.2502	Mn	0.05	8.12
CaO	0.13 ( $\pm 0.03$ )	—		Fe''	6.51	8 $\times$ 1.01
Na <sub>2</sub> O	0.14 ( $\pm 0.03$ )	—		H	29.09	8 $\times$ 3.64
K <sub>2</sub> O	0.09 ( $\pm 0.00^b$ )	—		O	78.92	8 $\times$ 9.87
H <sub>2</sub> O <sup>-</sup>	0.34 ( $\pm 0.02$ )	—				
H <sub>2</sub> O <sup>+</sup>	10.02	10.08	0.5595			
P <sub>2</sub> O <sub>5</sub>	—					
SO <sub>3</sub>	0.12	—				
F	tr. <sup>1</sup>					
V <sub>2</sub> O <sub>5</sub>	tr. <sup>2</sup>					
Total	100.26	99.99				

1. Ferrocapholite from cobble west of Tomata: average of duplicate analyses with deviations of separate analyses. Anal. Laboratorium voor Delfstoffenonderzoek van de Dienst van de Mijnbouw, Bandoeng (1949).

2. Analysis 1 recalculated to 100% after subtraction of CaO, Na<sub>2</sub>O, K<sub>2</sub>O, H<sub>2</sub>O<sup>-</sup> and SO<sub>3</sub>.

3. Ratios of 2.

4. Empirical unit-cell contents.

<sup>1</sup> Less than 0.02%.

<sup>2</sup> 0.011%.

tered in the determination of H<sub>2</sub>O<sup>+</sup> indicate that the water-content may be even higher than 10.02%.

According to the second spectrochemical analysis by Dr. Schmidt the main constituents are accompanied by traces of vanadium (more) and germanium (less).

Of the minor percentages recorded in the analysis, those which would require more or less unusual substitutions are within the limits of error to be expected for a normal chemical analysis (cf. Hillebrand and Lundell), and therefore have been omitted in the recalculated analysis. TiO<sub>2</sub> and MnO, which are commonly determined with greater accuracy, and which do not require unusual substitutions, have been retained.

The molecular weight of the unit-cell of ferrocapholite was calculated from the volume of the unit-cell and the density, both given in a later

part of this paper, and appeared to be 2600. The empirical unit-cell contents were found by multiplying the ratios for the recalculated analysis with 2600 and 0.01. According to its ionic radius Ti has been grouped together with Al and Fe''', accompanied by an equal amount of Mg (cf. Hallimond, page 70). Except for hydrogen, the empirical unit-cell contents thus obtained show good integral ratios. There are, however,

TABLE 2. ANALYSIS OF FERROCARPHOLITE COMPARED WITH THEORETICAL COMPOSITION AND WITH MODERN ANALYSES OF CARPHOLITE PROPER

	1	2	3	4	5	6
SiO <sub>2</sub>	37.38	36.79	38.68	35.73	36.07	42.14
TiO <sub>2</sub>	0.22	0.23	0.13	0.18	0.20	0.35
Al <sub>2</sub> O <sub>3</sub>	29.23	29.60	28.98	26.71	29.84	26.72
Fe <sub>2</sub> O <sub>3</sub>	2.06	2.09	3.02	2.02	1.36	2.71
Mn <sub>2</sub> O <sub>3</sub>	—	—	—	—	22.00	10.35
FeO	17.88	17.65	4.12	2.31	1.86	2.00
MnO	0.14	0.14	11.92	19.88	—	1.90
MgO	2.51	2.48	—	—	—	3.24
CaO	0.13	—	0.79	0.23	—	—
Na <sub>2</sub> O	0.14	—	0.30	—	—	0.22
K <sub>2</sub> O	0.09	—	—	—	—	0.16
H <sub>2</sub> O <sup>+</sup>	10.02	11.03	12.14	12.66	8.14	10.06
H <sub>2</sub> O <sup>-</sup>	0.34	—	—	—	—	0.15
SO <sub>3</sub>	0.12	—	—	—	—	—
F <sub>2</sub>	tr.	—	—	0.44	0.97	—
V <sub>2</sub> O <sub>5</sub>	tr.	—	—	—	—	—
	100.26	100.01	100.08	100.16	100.44	100.00
F <sub>2</sub> =O					0.41	
					100.03	

1. Ferrocapholite from cobble west of Tomata; results of analysis.
2. Theoretical composition of ferrocapholite with similar replacement ratios.
3. Carpholite, Wippra. Anal. H. Otto.
4. Carpholite, Schlaggenwald. Anal. H. Otto.
5. Carpholite, Schlaggenwald. Anal. J. Jakob.
6. Carpholite, Hettstedt. Anal. J. Jakob.

several arguments which indicate that the H-content of the unit-cell is 32 instead of 29. First, the difficulties encountered during the determination of H<sub>2</sub>O<sup>+</sup> indicate that the water-content may be higher, as mentioned above. A comparison with the analyses of carpholite proper by Otto and Jakob (see Table 2) indicates that Jakob encountered similar difficulties in the determination of the water-content; the deficient totals of his analyses, however, were attributed by Jakob to the presence of

$\text{Mn}_2\text{O}_3$ , an assumption which was later criticized by Otto, who obtained much higher figures for  $\text{H}_2\text{O}$ , i.e. 12.66% and 12.14%. Secondly, some water may have been lost during the drying in making the mineral separation. And lastly, the symmetry relations of the space-group *Ccca* indicate that the hydrogen-content of the unit-cell may be 28 or 32, with a much greater probability for the latter figure. Therefore, the water-content given in the analysis is assumed to be about 1% low (see Table 2) corresponding to 32 H atoms per unit-cell.

Thus, the formula obtained for ferrocarcholite may be written as  $\text{H}_4(\text{Fe},\text{Mg})\text{Al}_2\text{Si}_2\text{O}_{10}$ , the unit-cell containing 8  $\text{H}_4(\text{Fe},\text{Mg})\text{Al}_2\text{Si}_2\text{O}_{10}$ . The material from the vicinity of Tomata may be more exactly described as magnesian ferrocarcholite.

The density calculated from the cell-volume and the above formula, with minor replacements as given in the recalculated analysis, is 3.05, which is in good agreement with the measured value 3.04.

#### CRYSTALLOGRAPHIC PROPERTIES

The ferrocarcholite of the analyzed sample forms separate prismatic crystals and aggregates of parallel fibres with a length up to about 1 cm. The crystals are always elongated in the direction of the *c*-axis. In thin section the crystals do not show regular terminations.

According to the *x*-ray data given in a later part of this paper ferrocarcholite is orthorhombic dipyramidal, with  $a_0:b_0:c_0=0.682:1:0.253$ . During the investigation with the aid of the goniometer almost all crystals appeared to be very poorly developed or bent and almost all signals were very vague. In this respect ferrocarcholite corresponds to carpholite proper, on which almost no crystallographic measurements have been made. Observed crystal faces are:  $\{010\}$ ,  $\{100\}$  and  $\{110\}$ . The results of measurements on the best developed crystals observed are still unsatisfactory. They are given in Table 3.

TABLE 3. CRYSTALLOGRAPHIC MEASUREMENTS ON FERROCARCHOLITE

	$(010) \wedge (110)$	$(100) \wedge (110)$	$(010) \wedge (100)$
First crystal	$56^\circ 9'$	$33^\circ 53'$	$90^\circ 2'$
Second crystal	$55^\circ 39'$	$33^\circ 35'$	$89^\circ 33'$
	$56^\circ 11'$	$33^\circ 47'$	$89^\circ 47'$
	$56^\circ 11'$	$33^\circ 54'$	$89^\circ 59'$
	$56^\circ 14'$	$34^\circ 28'$	$90^\circ 42'$
Average	$56^\circ 5'$	$33^\circ 55'$	

The deviations from  $90^\circ$  of the values obtained for  $(010) \wedge (100)$  illustrate the great inaccuracy of the results of the measurements. According to the *x*-ray data, the angles of  $(110)$  with  $(010)$  and  $(100)$  are  $55^\circ 42'$

and  $34^{\circ} 18'$ ; the deviations of the values found by the author are supposed to be mainly due to the unsatisfactory development of the crystals. The values calculated from the x-ray data correspond very well with the values measured one hundred years ago by Kenngott for the prism angles of carpholite proper from Schlaggenwald:  $111^{\circ} 27'$  and  $68^{\circ} 33'$ .

The cross-sections of the prisms of the analyzed ferrocapholite often have the shape of rhombs with a truncation (100) of the obtuse angle (see de Roever 1947, Plate III, Fig. 2).

Twinning was not observed.

#### PHYSICAL PROPERTIES

The ferrocapholite from the vicinity of Tomata shows a dark green colour.

The crystals show a perfect cleavage according to  $\{010\}$ , while there is also an indistinct cleavage parallel to  $\{110\}$ . Furthermore the prisms may show a cross-parting.

Before the blowpipe the mineral melts more easily than actinolite and less easily than almandite. The fusibility is  $3\frac{1}{2}$ .

The mineral scratches fluorite and apatite but not orthoclase; therefore  $H=5\frac{1}{2}$ .

With the aid of the suspension method the specific gravity was found to be 3.04; the specific gravity of the heavy solution was determined by means of a Westphal balance, and checked with the aid of a pycnometer.

#### OPTICAL PROPERTIES

The refringence of the analyzed ferrocapholite is moderate; with the aid of the immersion method<sup>1</sup> a value of  $1.647 \pm 0.001$  was found for  $\gamma$  in sodium-light. The negative birefringence is rather strong; for  $\gamma-\alpha$  values of 0.019–0.020 were found with the aid of the Berek compensator and the universal stage, by comparison with quartz in thin section. For the partial birefringence  $\gamma-\beta$  values of 0.0033–0.0034 were found in two sections; for  $\beta-\alpha$  a value of 0.016 was measured in one section. From the determination of  $\gamma$ , of the birefringence and of the partial birefringences we find as approximate values for the other indices:  $\beta=1.644$  and  $\alpha=1.628$ . In one of the sections with the strongest birefringence some irregular cross-veins were observed with a slightly lighter color and with a birefringence that is 0.002 more than that of the main body of the crystal.

<sup>1</sup> With the aid of mixtures of  $\alpha$ -monochloronaphthalene and  $\alpha$ -monobromnaphthalene. The temperature could not be controlled; practically contemporaneous observations with microscope and refractometer were made at the same distance from the same sodium-flame.



For the optic axial angle  $2V_\alpha$  values of  $49^\circ$  were found in two sections with the aid of the universal stage. The same value was calculated from the above-mentioned figures for the refringence and the partial birefringences. The dispersion is weak,  $r > v$  with regard to  $\alpha$ .

The mineral shows parallel extinction in sections perpendicular to the optic bisectrices and the optic normal;  $\gamma$  is in the longitudinal direction of the crystals and  $\alpha$  in the longitudinal direction of the cross sections, i.e. perpendicular to the cleavage  $\{010\}$ . Consequently, the elongation is positive, (100) is the optic axial plane, and  $c = \gamma$ ,  $b = \alpha$  and  $a = \beta$  (see Fig. 1). In thin section the analyzed ferrocapholite shows a

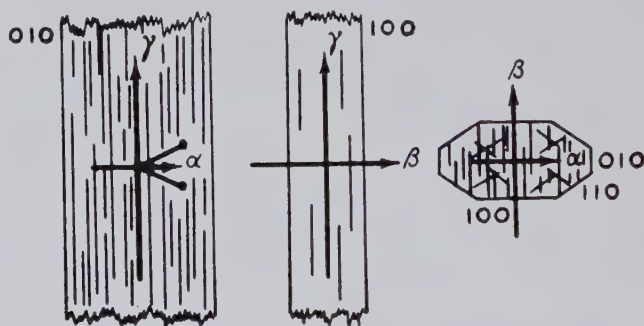


FIG. 1. Optic orientation of ferrocapholite.

distinct pleochroism from yellow-green ( $\alpha$  and  $\beta$ ) to very light blue-green ( $\gamma$ );  $\alpha$  and  $\beta$  show a very slight difference in color. The blue-green color of  $\gamma$  is distinctly observable in a slide with a thickness of about 0.035 mm.

Except for the colors in the sample and in thin section the optic characteristics of ferrocapholite (see also Table 5) correspond almost entirely with those reported for carpholite proper. Some recent optic data on carpholite proper are given for comparison in Table 4. In the literature the  $\gamma$  of carpholite proper is described as being colorless,<sup>1</sup> but carpholite from Wippra in the collection of the Geological Institute, Amsterdam, appeared in thicker sections to be of an extremely light bluish green color parallel to the  $c$ -axis.

#### X-RAY DATA

The cell-dimensions and the space-group of ferrocapholite were kindly determined in the laboratory of Prof. Dr. Carolina H. Mac Gil-

<sup>1</sup> According to Mügge, who also gives details on crystal faces and cleavage for carpholite proper, the absorption in the longitudinal direction is almost imperceptible in a thin section.

TABLE 4. OPTIC CHARACTERISTICS OF FERROCARPHOLITE COMPARED WITH THOSE OF CARPHOLITE PROPER ACCORDING TO MODERN DETERMINATIONS

	Ferrocarpholite, west of Tomata	Carpholite, Schlaggenwald (Jakob and) Hesemann	Carpholite, Schlaggenwald Larsen and Berman	Carpholite, Schlaggenwald Otto	Carpholite, Wippra Otto	Carpholite, Hettstedt (Jakob and) Hesemann
Color in sample	dark green	straw-yellow	straw-yellow			greenish yellow
Pleochroism	very light blue-green to yellow-green	colorless to pistachio-green	colorless to pale yellow			colorless to golden yellow
Indices						
$\gamma$	1.647	1.639	1.630	1.632	1.637	1.638
$\beta$	1.644	1.632	1.628	1.630		1.631
$\alpha$	1.628	1.617	1.611	1.613	1.619	1.612
Birefringence	0.019–0.020	0.0215	0.019	0.019	0.018	0.028
$2V_{\alpha}$	$49^{\circ}$	$70^{\circ}$	$50^{\circ}$			$62^{\circ}$

lavry, Amsterdam, to whom the author expresses his sincere thanks.

For the cell-dimensions the following results were obtained:  $a_0 = 13.77 \text{ \AA}$ ,  $b_0 = 20.18 \text{ \AA}$ ,  $c_0 = 5.11 \text{ \AA}$ . For carpholite proper the only value known is that of  $c_0 = 5.3$  according to a preliminary determination by Strunz, who concluded that carpholite belongs to his group of inosilicates with endless chain structures. The same may hold true for ferrocarpholite.

Weissenberg diagrams of the zero and first layer line around the  $c$ -axis, and of the zero layer line around the  $a$ -axis, show the space-group to be  $Ccca = D_{2h}^{22}$ .

From a fibrous specimen of carpholite proper from Wippra a rotation diagram was made. A comparison of this diagram with a rotation diagram of a single crystal of ferrocarpholite shows that the two structures are isomorphous.

A full structure determination is in progress in Prof. Mac Gillavry's laboratory.

## OCCURRENCE

The analyzed ferrocapholite, which was found in a cobble of vein-quartz west of Tomata, is further accompanied by red ore-material and by very small quantities of rutile, leucoxene, zircon and tourmaline.

In two other samples from eastern Central Celebes investigated by the author practically manganese-free carpholite-like minerals are of subordinate or local occurrence. These are a blastopsammitic schistose biotite- and chlorite-bearing sericite-quartzite with quartz veins containing the said mineral (No. 17-47<sup>x</sup>), and a blastopsephitic sericite-quartzite (No. 17-42), both collected in situ by Prof. Dr. H. A. Brouwer, east of Tamondjengi, north of the trail to Majoemba, and SW. of Peleroe on the trail to Majoemba.<sup>1</sup>

TABLE 5. OPTIC CHARACTERISTICS OF FERROCAPHOLITE COMPARED WITH THOSE OF OTHER PRACTICALLY MANGANESE-FREE CARPHOLITE-LIKE MINERALS FROM EASTERN CENTRAL CELEBES

	Ferrocapholite, west of Tomata, 15-161 <sup>x</sup>	SW. of Peleroe, 17-42	East of Tamondjengi, 17-47 <sup>x</sup>
Color in sample	dark green	gray-green to green	gray-green to green
Pleochroism			
$\gamma$	very light blue-green	extremely light bluish green	extremely light bluish green
$\beta$	yellow-green	light yellow-green or light green-yellow	green-yellow
$\alpha$	yellow-green	light green or light yellow-green	green-yellow
Indices			
$\gamma$	1.647	1.640	1.638
$\beta$	1.644	1.636	1.633
$\alpha$	1.628	1.621	1.617
Birefringence	0.019-0.020	0.019	0.020-0.021
2V <sub><math>\alpha</math></sub>	49°	55°-57°	60°-61°
Orientation	$c = \gamma$ $b = \alpha$ $a = \beta$	$c = \gamma$ $b = \alpha$ $a = \beta$	$c = \gamma$ $b = \alpha$ $a = \beta$

<sup>1</sup> For the exact position of the localities mentioned the reader is referred for the author's paper on the igneous and metamorphic rocks from eastern Central Celebes, page 72.

Since the refringence and other optical characteristics of the minerals in these samples are close to those of ferrocarpholite (see Table 5), while the content of manganese is negligible in comparison with that of carpholite from Wippra, we may also be dealing here with magnesian ferrocarpholite, which in view of its lower refringence may have a larger content of magnesium. The minerals are associated with quartz, sericite, biotite, chlorite, hematite, leucoxene, tourmaline, rutile and zircon. In one of these rocks some crystals of zircon were found as inclusions in the carpholite-like mineral; around the crystals of zircon no diverging optical characteristics of the carpholite-like mineral were observed.

In all localities mentioned the mineral occurs in veins in or as a constituent of low grade metamorphic phyllitic and quartzitic rocks, among which some original sandstones and conglomerates could be recognized. The metamorphism of these rocks is of alpine age and may belong to the greenschist facies, which in other parts of Celebes was found to be younger than the wide-spread glaucophanitic metamorphism of the eastern part of this island. It is not impossible, however, that these low grade metamorphic rocks belong to a facies characterized by the stability of pumpellyite, or to the glaucophane-schist facies itself.

For further details the reader is referred to the author's paper on the igneous and metamorphic rocks from eastern Central Celebes.

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# IMMERSION LIQUIDS OF HIGH REFRACTIVE INDEX\*

ROBERT MEYROWITZ AND ESPER S. LARSEN, JR.

## ABSTRACT

A new series of high-index immersion liquids (1.74 to 2.00) has been made. Methylene iodide and a solution of precipitated sulfur (10 per cent) in arsenic tribromide are the end members of the liquids between 1.74 and 1.81. The mixing curve is not a straight line. The end members of the liquids from 1.82 to 2.00 are a solution of precipitated sulfur (10 per cent) in arsenic tribromide, and a solution of precipitated sulfur (20 per cent) and arsenic disulfide in arsenic tribromide (60 per cent). This mixing curve is a straight line.

The temperature coefficient of the liquids is of the same order of magnitude as that of methylene iodide but the dispersion is higher. After six months the maximum change in index of the liquids between 1.74 and 1.81 was  $\pm 0.001$ . For the liquids between 1.82 and 2.00 it was  $\pm 0.003$ .

Liquids of various combinations have been made from arsenic tribromide, arsenic disulfide, arsenic trisulfide, sulfur, selenium, mercuric sulfide, antimony bromide, and  $\alpha$ -bromonaphthalene. The highest index obtained was 2.1 for a mixture of arsenic tribromide, arsenic disulfide, and selenium.

## INTRODUCTION

A study of inorganic, organic, and metal-organic compounds that might be employed in the preparation of high refractive index liquids is in progress at the U. S. Geological Survey. It is part of a program of research in the geochemistry of uranium which the Survey is undertaking on behalf of the Atomic Energy Commission.

As part of this study, a new series of immersion liquids that range in index from 1.74 to 2.00 has been made. The 1.74 to 1.81 liquids contain methylene iodide, precipitated sulfur, and arsenic tribromide. Those from 1.82 to 2.00 contain arsenic tribromide, precipitated sulfur, and arsenic disulfide.

It is now six months since complete sets of these liquids were made and distributed for testing. The favorable comment of the mineralogists and petrologists who have used them, and the interest in them that others have shown, warrants their introduction for general use so early in their development.

The authors intend to present a complete report on this series of liquids after they have been in use for at least a year. Meanwhile, a brief description of the liquids, together with their limitations and the method that has been used for their preparation, are presented here. These liquids are a further development of the arsenic tribromide liquids described by L. H. Borgström (1929, 1933) of Finland.

The liquids containing methylene iodide, sulfur, and arsenic tribromide

\* Publication authorized by the Director, U. S. Geological Survey.



were originally yellow amber in color but darkened on standing because of the decomposition of methylene iodide. The liquids containing arsenic tribromide, sulfur, and arsenic disulfide range in color from yellow to dark amber.

A disadvantage inherent in all liquids containing arsenic tribromide is its acidic properties *per se* and the fact that it forms by hydrolysis with water or water vapor hydrobromic acid and a white precipitate of arsenic trioxide. Because of their acidic nature these liquids will react with some minerals. The corrosion of metals can be avoided by taking the proper precautions, and the effect of hydrolysis can be made negligible by making the immersion rapidly. The liquid when covered quickly by a coverslip will remain stable. These liquids must be stored in glass bottles with a ground-glass stopper and a ground-glass dust cover.

Some of the liquids have developed a slight turbidity. This turbidity is due to the presence of very fine grained crystals which are not objectionable in ordinary immersion work. The 1.98, 1.99, and 2.00 liquids were supersaturated with respect to sulfur when originally prepared. It takes some time for these high-index liquids to come to equilibrium. The sulfur that precipitates from solution will be in the form of relatively large crystals that can be removed easily by filtration through sintered glass. The liquid itself remains clear. The 1.80, 1.81, and 1.82 liquids may become solid if the temperature at which they are stored falls much below that of normal room temperature (20° to 25° C.). Gentle warming will effect complete solution and after thorough mixing the clear liquid will have its original refractive index.

After a period of six months the maximum change in index of the liquids between 1.74 and 1.81 was  $\pm 0.001$ ; for the liquids between 1.82 and 2.00 it was  $\pm 0.003$ .

The temperature coefficient ( $dn/dT$ ) of the liquids between 1.74 and 1.81 is  $7 \times 10^{-4}$ . That of the rest of the series is  $6 \times 10^{-4}$ . The dispersion, as measured by the difference in index between the "e" line of mercury (546) and the "D" line of sodium (589), is as follows:

$\alpha$ -bromonaphthalene.....	$76 \times 10^{-4}$
Methylene iodide.....	$88 \times 10^{-4}$
1.74 liquid.....	$96 \times 10^{-4}$
1.81 liquid.....	$103 \times 10^{-4}$
1.83 liquid.....	$116 \times 10^{-4}$
2.00 liquid.....	$174 \times 10^{-4}$

## PREPARATION OF IMMERSION LIQUIDS

### *Liquids between 1.74 and 1.81*

*Reagents.*—1. Methylene iodide, Eastman Organic Chemical No. 167

supplied by Distillation Products Industries, Rochester 3, N. Y.

2. Sulfur, precipitated, U.S.P.

3. Arsenic tribromide, C.P., supplied by A. D. Mackay, Inc., 198 Broadway, New York 7, N. Y.

The end members are:

1. Methylene iodide,  $n_{\text{Na}}^{25^\circ \text{C}} = 1.738$

2. 10 per cent sulfur in arsenic tribromide,  $n_{\text{Na}}^{25^\circ \text{C}} = 1.814$

*Preparation of solution of 10 per cent sulfur in arsenic tribromide.*—The sulfur and arsenic tribromide (10:90 by weight) are mixed in a glass-stoppered Erlenmeyer flask and solution is effected by gentle warming. After standing at room temperature overnight, the solution is filtered by suction through a sintered glass of "medium" porosity. The filtrate is passed through the same filter until it is no longer turbid.

The mixing curve obtained with the two end members deviates considerably from a straight line, and the curve may be constructed from the following table.

10 per cent S in AsBr <sub>3</sub> (in grams)	Methylene iodide (in grams)	$n_{\text{Na}}^{25^\circ \text{C.}}$
5.4	174.6	1.742
21.6	158.4	1.753
36.9	143.1	1.762
52.2	127.8	1.771
71.1	108.9	1.781
92.7	87.3	1.792
119.7	60.3	1.801
158.4	21.6	1.811

The necessary amounts by weight of the high and low end members are mixed together in glass-stoppered bottles or Erlenmeyer flasks to obtain the series of liquids of desired intervals. The refractive indices of the liquids are determined after thorough mixing.

#### *Liquids between 1.82 and 2.00*

*Reagents.*—1. Sulfur, precipitated, U.S.P.

2. Arsenic tribromide, C.P.

3. Arsenic disulfide, C.P., supplied by A. D. Mackay, Inc., 198 Broadway, New York 7, N. Y.

The end members are:

1. 10 per cent sulfur in arsenic tribromide,  $n_{\text{Na}}^{25^\circ \text{C}} = 1.814$

2. A solution of sulfur and arsenic disulfide in arsenic tribromide whose composition is 20:20:60 by weight,  $n_{\text{Na}}^{25^\circ \text{C}} = 2.003$ . These end members have a straight-line mixing curve.

*Preparation of solution of sulfur and arsenic disulfide in arsenic tribromide.*—To 60 parts by weight of arsenic tribromide in a glass-stoppered Erlenmeyer flask are added 20 parts by weight of sulfur. The mixture is warmed gently to effect solution. Then 20 parts by weight of powdered arsenic disulfide are added and the mixture is heated over a small flame, mixing constantly until a temperature of 100° C is reached. Heating is continued for 5 minutes, keeping the temperature of the mixture between 100° and 120° C. During the entire heating period the liquid is constantly mixed.

After standing at room temperature overnight, the solution is filtered by suction through sintered glass of "medium" porosity. The filtration will be very slow because of the high viscosity of the liquid. The filtrate may be slightly turbid.

The necessary amounts by weight of the high and low end members are mixed together in glass-stoppered bottles or Erlenmeyer flasks to obtain the series of liquids of desired intervals. The liquids are mixed thoroughly.

Each liquid is filtered by suction through sintered glass of "fine" porosity. The first portion of the filtrate may be slightly turbid. If so, the filtrate is passed through the same filter until it is clear. The refractive indices of the liquids are determined after thorough mixing.

The solutions or mixtures should be kept covered as much as possible during the preparation of all solutions containing arsenic tribromide because of the hydrolysis of arsenic tribromide by the water vapor in the air.

Liquids of various combinations have been made from arsenic tribromide, arsenic disulfide, arsenic trisulfide, sulfur, selenium, mercuric sulfide, antimony bromide, and  $\alpha$ -bromonaphthalene. The highest index obtained was 2.1 for a mixture of arsenic tribromide, arsenic disulfide, and selenium.

The results of this study of compounds that might be used in the preparation of high refractive index liquids will be given in a series of reports, one of which will be a history and annotated bibliography of high-index immersion liquids and another a discussion of some theoretical aspects of liquids of high refractive index and the compounds they contain.

The cost of the materials used in the preparation of a set (1.74 to 2.00) of 27 immersion liquids, each containing 8 ml of liquid, is approximately \$50. The price of the bottles to hold these liquids is about half this amount. This estimate is based on January 1950 prices of reagents and bottles which are as follows:

Arsenic tribromide, C.P.....	\$13.00 per lb.
Sulfur, precipitated, U.S.P.....	0.55 per lb.

Methylene iodide, pure.....	4.50 per 100 g.
Arsenic disulfide, C.P.....	13.33 per lb.
Bottles, dropping, with solid glass stopper drawn to a fine point for dropping, with glass cap ground on, 15-ml. capacity.....	0.65 each

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## BERYL AT MOUNT MICA, MAINE\*

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### ABSTRACT

In 1949 a new pocket was opened at Mount Mica which appears to be on the projected strike and dip of the zone of the old pockets which contained gem tourmaline. In the new pocket, beryl crystals of unusual habit were found with milky cores and colorless exterior. It is believed that cores were derived by the shattering of large crystals on the wall of the pocket and that the later colorless beryl was deposited in such a way as to preserve as nearly as possible the shape of the fracture fragments. Chemical analyses of both types of beryl are given.

### EARLY WORKINGS AT MOUNT MICA

Gem tourmaline was discovered in the pegmatite on Mount Mica in 1820. From that time until 1864 there were only desultory attempts at mining, although the locality was visited by many geologists and mineralogists. In 1864 active work was commenced which continued intermittently until 1913. For a short time in 1873 mining was carried on for muscovite and between 3,000 and 4,000 pounds of mica were removed. Aside from the mica mining, the activity was entirely a search for pockets containing gem tourmaline. The operations were of doubtful financial success, but they did produce a large number of beautiful gem tourmalines which make Mount Mica a world-renowned mineral locality.

An interesting account of the work up to 1895 and a description of some of the finest gems are given by Hamlin in his book, *The History of Mount Mica*. Bastin† discusses the mineralogy of the pegmatite and describes the later work up until 1910. He also gives a brief account of the geology; a portion of which is as follows:

"... the Mount Mica pegmatite mass dips gently 20° to 30° SE., being intruded in general parallel to the trend of quartz-mica schists, which at the quarry strike N. 50° to 60° E. and dip 20° to 30° SE. . . .

"The whole pegmatite mass is not productive, the gem and pocket bearing portion constituting a zone ranging from a few inches to 6 or 7 feet in thickness lying immediately below the schist capping. The productive layer originally outcropped at the surface, a relation to which was due its discovery and the ease with which it was worked in the early days. At present the southeastern wall of the quarry is capped by about 10 to 15 feet of schist which must be stripped off before the pocket-bearing zone is reached."

\* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 329.

† Geology of Pegmatites of Maine; *U. S. Geol. Survey, Bull.* 445 (1911).



Subsequent to the operations reported by Bastin, workings were extended only slightly to the northwest and in 1913 the last pocket containing tourmaline was opened. Mining came to an end when it became too costly to remove the overlying schist for further exploration down the dip. The workings, essentially the same to-day as they were then, are shown diagrammatically in Fig. 1.

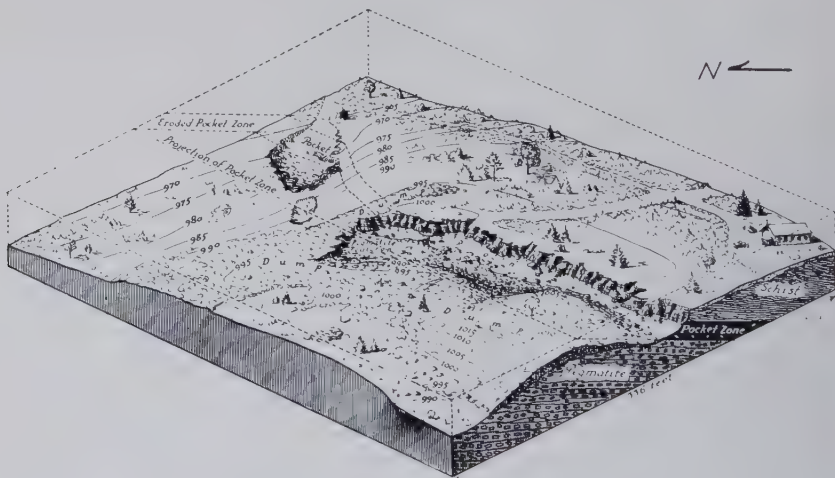


FIG. 1. Block diagram of Mount Mica. Topography by Robert Miller and Lawrence Wing. Maine Geological Survey, Maine Development Commission, 1943.

### THE NEW POCKET

To the northeast of the old workings quarrying operations for feldspar have been undertaken in recent years where the slope of the hill exposes the pegmatite at the surface. No pockets were encountered until June 1949 when the operations of the United Feldspar Company broke into a cavity—the second largest to be found at Mount Mica.

Neglecting minor irregularities and assuming that the pocket zone of the pegmatite is a sheet 7 feet thick striking N. 55° E. and dipping 25° SE., this new pocket lies within the same horizon (Fig. 1). Its presence may well indicate an extensive continuation of the pocket zone under the southeast slope of Mount Mica.

Although the new pocket lies along the projected strike and dip of the zone containing the old workings, its relation to the schist is quite different. Fifteen feet of pegmatite, composed mostly of microcline and quartz, overlie the pocket and extend to the surface with no schist above. It may well be that this overlying pegmatite is a separate injection intruded between the pocket zone and the schist and it is in this

upper pegmatite that the recent feldspar operations have been carried out.

The new pocket was about 20 feet long, 5 feet wide and 4 feet high with the longest dimension essentially horizontal with a NW-SE strike. The largest pocket in the old workings measured  $20' \times 12' \times 7'$ . The day before the pocket was actually broken open, drilling indicated its presence. After penetrating about two feet below the quarry surface, a drill dropped several feet into the cavity. When, in another hole six feet away, the drill reached the same depth, it likewise dropped and water



FIG. 2. Southeast end of the pocket exposed by deepening of the quarry floor. The main portion of the pocket extended into the foreground.

spouted several feet in the air from the first hole. Because of this advanced notice, the writers were able to be present on the following day when a blast made a small opening into the northwest end of the water-filled pocket.

Initial exploration carried out by reaching arm's length into the hole yielded nothing of unusual interest. The roof was covered with sub-parallel books of muscovite 4 to 5 inches in diameter with the platy edges projecting downward. On the sloping floor were fragments of feldspar and a few imperfect quartz crystals. Just within reach was a large loose crystal which proved to be a deeply etched Baveno twin of microcline  $10 \times 8 \times 8$  inches. No lepidolite nor cleavelandite was noted

either inside the pocket nor in the rock surrounding it. In the old workings these minerals were usually encountered in the vicinity of gem-bearing pockets.

When the pocket was eventually opened for complete inspection, the writers could not be present but most of the contents gathered from the floor were made available to them through the courtesy of the owner, Mr. Howard Irish of Buckfield, Maine. In addition to the books of muscovite on the walls and roof of the pocket, there were large areas covered by a subparallel aggregate of albite crystals. No tourmaline was found and thus this pocket would have been declared barren by the early workers at Mount Mica.

#### BERYL CRYSTALS

The contents of the pocket gathered from the floor amounted to about two bushels of small crystals (four inches and under) mostly quartz. In addition there were several larger smoky quartz crystals; the largest, 18 inches long and 10 inches wide, was well formed. On the floor at the southeast end of the pocket were many colorless to milky white beryl crystals of such unusual habit that their identity was not immediately apparent. They ranged from  $\frac{1}{2}$  inch to 8 inches in length and the majority were covered with crystal faces. Their most remarkable feature was the complete individuality of each crystal. No two were alike in shape nor in development of forms and none showed the prismatic habit characteristic of most beryl.

*Morphology.* In spite of the large size of many of the crystals, most of the faces were sharp and gave usable signals on the reflecting goniometer. Only in determining the angular measurements of the largest crystal was recourse made to the contact goniometer. This crystal measured  $8 \times 3 \times 2$  inches and weighed three pounds (Fig. 6). Because of the high quality of the faces, one felt justified in having faith in the angular measurements even though the resultant indices are unusual. On many crystals a form with high indices is represented by only one face, but it, as  $(\bar{7} \cdot 14 \cdot \bar{7} \cdot 8)$  in Fig. 5 is a major face. Table 1 lists the forms and compares measured with calculated angles. The frequency of occurrence and distribution of forms on the fourteen crystals measured is also indicated. Of the thirty forms included in the table, seventeen (marked with an asterisk) are not listed by Goldschmidt\* or Whitlock.†

From Table 1 it can be seen that certain forms such as  $\{0001\}$ ,  $\{10\bar{1}0\}$ ,  $\{11\bar{2}1\}$  and  $\{21\bar{3}1\}$  are usually present. However, the size of the faces of

\* Goldschmidt, V., *Atlas der Krystallformen*, Heidelberg (1913).

† Whitlock, H. P., A List of New Crystal Forms of Minerals: *Bull. Am. Mus. Natl. Hist.*, XLVI (1922).

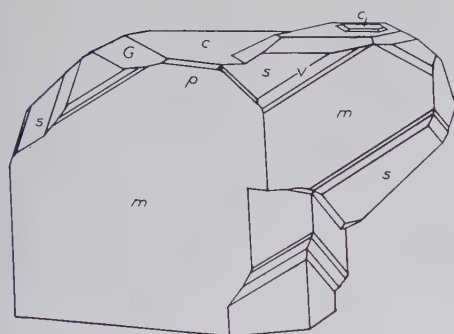


fig 3

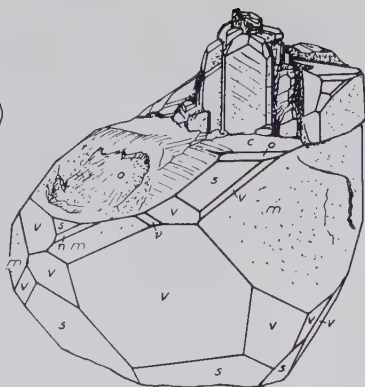
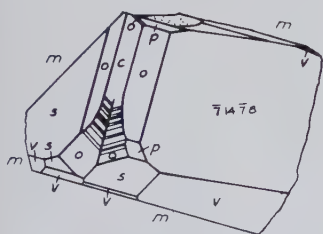
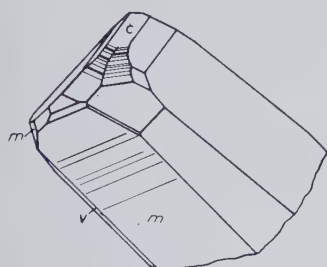


Fig 4



(a)



(b)

Fig 5

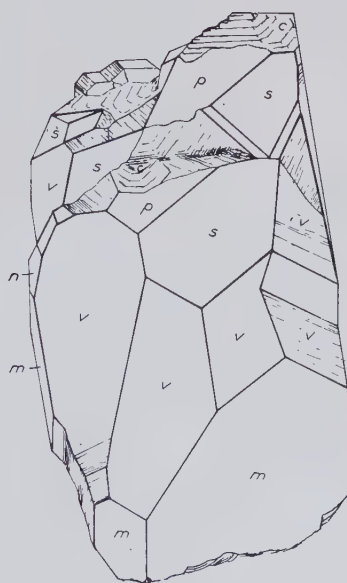


Fig 6

FIGS. 3, 4, 5, 6. Beryl crystals, Mount Mica. Fig. 5(a) Orthographic projection of the same crystal shown in clinographic projection in Fig. 5(b).

TABLE 1. MOUNT MICA BERYL: TWO-CIRCLE MEASUREMENTS

Form	Measured		Calculated ( $P_0 = 0.5762$ )		Num- ber of Faces	Num- ber of Crys- tals
	$\phi$	$\rho$	$\phi$	$\rho$		
0001	—	0°00'	—	0°00'	14	12
10 $\bar{1}$ 0	29°50'–30°04'	89°50'–90°04'	30°00'	90°00'	81	14
10 $\bar{1}$ 1	29°53'–30°02'	29°54'–29°58'	30°00'	29°57'	8	3
*7074	29°57'–30°00'	47°20'–47°23'	30°00'	47°23'	3	2
*8083	29°58'–30°01'	49°00'–49°04'	30°00'	49°03'	3	2
*16·0· $\bar{1}$ 6·3	29°59'	71°57'	30°00'	71°58½'	1	1
1126	359°54'– 0°05'	9°20'– 9°30'	0°00'	9°27'	4	2
*1124	359°47'– 0°04'	13°50'–14°02'	0°00'	14°00'	15	3
1123	359°55'– 0°03'	18°10'–18°31'	0°00'	18°24'	17	5
*2245	0°01'– 0°13'	21°45'	0°00'	21°46'	3	1
1122	357°56'– 0°05'	26°14'–26°46'	0°00'	26°31'	19	4
*7·7· $\bar{1}$ 4·8	0°04'	41°06'	0°00'	41°08'	1	1
1121	359°50'– 0°07'	44°18'–45°20'	0°00'	44°56'	50	11
*4376	4°40'– 4°44'	30°15'–30°18'	4°43'	30°17½'	2	2
*3256	6°34'– 6°38'	22°33'–22°49'	6°35'	22°43'	8	2
2133	10°52'	26°54'	10°53½'	26°56'	2	1
2131	10°28'–10°59'	56°30'–57°11'	10°53½'	56°44'	88	12
*7·3· $\bar{1}$ 0·3	12°59'–13°04'	59°30'–59°43'	13°00'	59°38'	8	1
5272	13°50'–13°53'	60°50'–60°56'	13°54'	60°56'	6	3
*33·11· $\bar{4}$ 4·6	16°00'–16°05'	75°15'–75°18'	16°06'	75°17'	7	1
*4151	19°10'–19°24'	69°03'–69°20'	19°06½'	69°15½'	4	2
*9·2· $\bar{1}$ 1·2	20°10'–20°19'	71°00'–71°09'	20°10½'	71°07'	10	2
*19·4· $\bar{2}$ 3·4	20°29'–20°35'	71°54'–72°01'	20°38'	71°56'	19	4
5161	21°01'–21°09'	72°39'–72°44'	21°03'	72°41'	9	1
6171	22°24'–22°28'	75°01'–75°14'	22°24½'	75°11'	6	2
*13·2· $\bar{1}$ 5·2	22°53'	76°09'	22°57'	76°11'	1	1
*8191	24°12'–24°16'	78°34'	24°11'	78°31'	2	1
13·1· $\bar{1}$ 4·1	26°20'–26°22'	82°39'–82°45'	26°20'	82°41'	4	1
*14·1· $\bar{1}$ 5·1	26°37'	83°05'–83°11'	26°35'	83°34'	4	1
*60·3· $\bar{6}$ 3·4	27°38'–27°42'	83°30'–83°41'	27°41'	83°34'	8	1

\* New forms.

these forms on the different crystals varies widely; on some they may be major faces, whereas on others they are extremely minor. All crystals on which {1122} was found showed curved surfaces between the faces of this form and {0001}. Some of the forms, particularly those with high indices, seemed open to question after the first measurement. All, however, have been checked by remeasurement. Four additional forms were considered uncertain and are not included in Table 1.

*Zoning.* All of the beryl crystals are zoned with a core of milky material



and a colorless, glassy exterior. By looking through the colorless portion one can observe well the contact between the two zones. In most crystals this contact is not parallel to crystal faces as is commonly seen in ghost crystals, but is a rough fracture surface without crystallographic orientation. On one crystal which was sawed in two, a small cavity was present between the two zones exposing the original fracture surface (see Fig. 7). The evidence indicates, therefore, that the cores are rough fragments broken from earlier formed beryl and that the glassy exterior was added later.

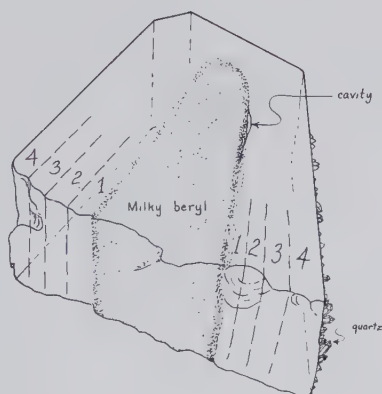


FIG. 7. Section sawed from crystal illustrated in Fig. 5. Numbers indicate the locations of samples taken for spectrographic analysis.

Covering a portion of the wall of the pocket in the vicinity of the crystals, beryl in coarse columns about three feet long was found sloping toward the center of the pocket at an angle of  $45^\circ$ . This coarse beryl corresponds exactly to the material of the cores of the smaller crystals; it is milky white and has the same specific gravity and refractive indices. It appears likely that the columnar beryl was shattered and fragments of it fell to the floor of the pocket where they acted as nuclei for the deposition of the later transparent beryl. Moreover, the columnar beryl on the surfaces exposed in the pocket is covered with clear material exhibiting many crystal faces, and cracks within it have been healed with the same colorless beryl.

The unusual habit of the smaller crystals appears to be due to the irregular shape of the fragments which acted as cores. The late transparent beryl was deposited on the cores with a tendency to form crystal faces as nearly parallel to the fracture surfaces as possible. This accounts for the extraordinary habits and the fact that one face of a form may be large and the other faces poorly developed or absent. On a few of the

crystals one or two prism faces have little or none of the later material deposited upon them, and represent the original prism faces of the columnar beryl.

The cores of milky beryl are very uniform in composition as indicated by constant indices of refraction and specific gravity. The milky beryl owes its cloudy appearance to many microscopic cavities and their presence undoubtedly accounts in part for the very low specific gravity. ( $G=2.650$ )

The transparent beryl of the exterior, on the other hand, shows a wide variation in its properties. Attempts to determine the indices of refraction by the method of minimum deviation on cut prisms yielded erratic and variable values which were not in agreement with earlier values obtained by the double variation method. Although the clear beryl coatings were apparently homogeneous and displayed no obvious

TABLE 2. ALKALI CONTENT, REFRACTIVE INDICES AND SPECIFIC GRAVITIES OF MOUNT MICA BERYL

Sample	Total* Alkalis	Spectrographic Analysis**				(Na) Refractive Index		Sp. Gr.
		Cs	Li	Rb	K	O	E	
Milky	0.84	0.15	0.6-0.8	0.04	tr	1.580	1.574	2.650
1	1.07	0.1	0.1	0.05	tr	1.573	1.568	2.675
2		0.15	0.1	0.05	tr	1.580	1.574	2.692
3		1.0	0.5	0.05	tr	1.598	1.591	2.780
4		2 to 6	1.0	0.1	tr			

\* F. A. Gonyer, analyst.

\*\* H. C. Harrison, analyst.

evidence of zoning, compositional variation was suspected. Small fragments were broken from the clear zone of a sawed slab and the indices determined by immersion. The specific gravities of similar fragments, ten to fifteen milligrams in weight, broken from the inner, outer and middle portions of the clear beryl layer, were obtained on the Berman balance. An increase in refractive indices and specific gravity from the milky core outward is clearly shown (Table 2). Because of the continuous nature of the change and the relatively thin coating of clear beryl (5 mm. maximum), it is impossible to obtain even a small fragment of uniform composition. Consequently, it is probable that neither the high nor the low extreme in specific gravity is represented by the values given below. Moreover, the refractive indices as given should be considered merely as the mean of the zone they represent.

By the use of a small diamond drill, four separate channel samples of

the clear beryl were obtained for spectrographic analysis from the crystal shown in Fig. 5. The locations from which these samples were removed are shown in Fig. 7. Semiquantitative spectrographic analysis shows a progressive increase in cesium and lithium from the innermost zone outward. There is a concomitant, but much less clearly marked, increase in rubidium, while potassium is present only as a trace in all samples.

*Chemical Analysis.* Analyses of both the clear and milky beryl were made by F. A. Gonyer. Analysis 1 represents merely the average composition of the clear beryl, for no attempt was made to separate the zones. The chief differences in the two beryls are shown in the higher percentage of alkalis and the lower percentage of BeO in the clear beryl.

TABLE 3. CHEMICAL ANALYSES OF BERYL FROM MOUNT MICA

	Clear Beryl 1	Milky Beryl 2
SiO <sub>2</sub>	64.54	64.80
Al <sub>2</sub> O <sub>3</sub>	18.51	18.38
BeO	13.20	14.68
Li <sub>2</sub> O	0.86	0.68
Na <sub>2</sub> O	1.12	0.76
K <sub>2</sub> O	0.21	0.16
Rb <sub>2</sub> O		
Cs <sub>2</sub> O		
H <sub>2</sub> O	1.24	0.78
Total	99.68	100.24

*Cell Dimensions.* X-ray powder photographs were made on the same samples of clear beryl used for spectrographic analysis. Back reflection lines in the region  $2\theta = 145^\circ$  to  $170^\circ$  were compared in a search for a systematic variation in cell dimensions with changes in alkali content. The variations found lie within the estimated limits of experimental error and it is concluded that no systematic change in cell dimensions has accompanied the wide variation in alkali content indicated in the table above. For example, the spacing for a line in the region  $2\theta = 145^\circ$  was determined as  $d = 0.8081 \text{ \AA} \pm .0001$  for the inner zone,  $d = 0.8081 \text{ \AA} \pm .0001$  for the intermediate zone,  $d = 0.8082 \text{ \AA} \pm .0001$  for the outer zone (samples 3 and 4 combined). The  $d$  values above represent the mean of calculated values based on measurement of both  $\text{CuK}\alpha_1$  and  $\text{CuK}\alpha_2$  lines.

The writers wish to acknowledge the help given by Dr. Howard T. Evans and Mr. David B. Stewart in the preparation of some of the crystal drawings.

## SOME ASPECTS OF MINERAL CALORIMETRY

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### ABSTRACT

An empirical expression was established relating the thermographic response and heating rate of a differential thermal analyzer. As a result, accurate calorimetric measurements are made at heating rates between 10° C and 30° C per minute.

Samples of large mass are to be avoided when measuring small heat changes by differential thermal analysis. A simple experiment gave a relation between sample mass and thermographic response which indicated that precise calorimetric measurements are made by first determining the optimum mass of the sample to be tested.

### INTRODUCTION

The recent improvements of differential thermal apparatus<sup>1</sup> have led to the development of refined heat-measuring techniques. As a result many mineralogic transformations can be detected and energies of transformation accurately measured. A calibration of one of these instruments for micro-calorimetric purposes was described in a recent issue of this journal.<sup>2</sup> In the discussion of that calibration two important features were emphasized: (1) the use of high heating rates, and (2) the testing of samples of small mass.

Subsequent investigation of the thermal characteristics of the apparatus indicated that a more precise relationship exists between the thermographic response and the two features above. An empirical expression was established relating heating rate and thermographic response. In addition, the effect of sample mass on thermographic response was experimentally determined. The conclusions reached in the earlier investigation are upheld by the analysis described below.

### RELATION BETWEEN HEATING RATE AND THERMOGRAPHIC RESPONSE

Three additional calibrations of the apparatus were made at heating rates slower than 30° C per minute by the same method described in the earlier investigation. The results of the calibration for the four heating rates are graphically shown in Fig. 1. A cursory examination of this plot reveals that some regular relation exists between the rate of heating

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<sup>1</sup> Whitehead, W. L., and Breger, I. A., Vacuum differential thermal analysis: *Sci.*, **111**, 279-281 (1950).

<sup>2</sup> Wittels, M., The differential thermal analyzer as a microcalorimeter: *Am. Mineral.*, **36**, 615-621 (1951).

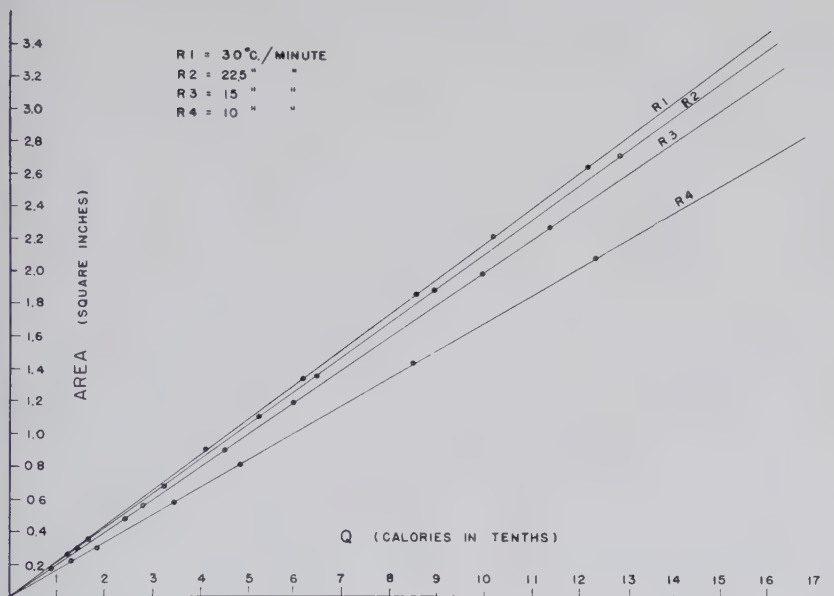


FIG. 1. Thermographic response for four rates of heating.

and the corresponding thermographic responses for a given energy change.

In order to obtain a clearer picture of this relation the following terms are first defined.

From Fig. 1,

$A$  = Area

$Q$  = Calories

$\theta = \tan^{-1} \left( \frac{A}{Q} \right)$  measured in degrees and tenths on scale of Fig. 1.

$R$  = Rate of heating

$$Q = \frac{A}{\tan \theta} \quad (1)$$

The use of units in the above terms are prohibitive in the derivations following, obviously, because the numerical values are strictly relative, e.g. square inches versus calories in Fig. 1.

The graphical representation of  $R$  and  $\theta$  in Fig. 1 indicates that some form of exponential relation exists between these two functions. A plot of  $R$  versus  $\theta$  (Fig. 2) as compared to the plot of  $e^x$  against  $x$  verifies this



observation. The values for  $R$  and  $\theta$  are tabulated below.

$R$	$\theta$
10	30.17
15	34.50
22.5	36.00
30	36.92

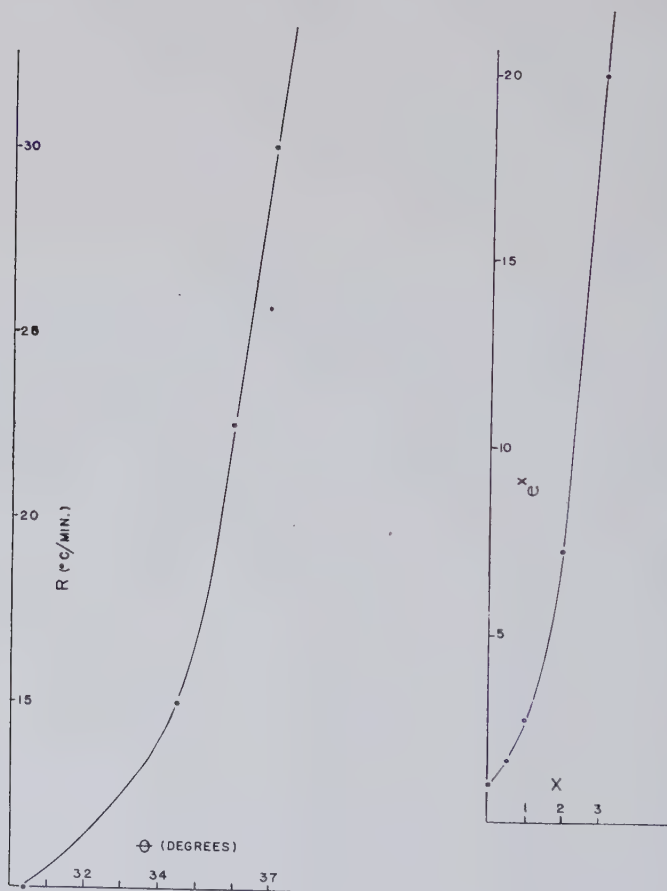


FIG. 2. Relation between  $R$  and  $\theta$ .

We shall now proceed to find the relation between  $R$  and  $\theta$  so that some function of  $R$  can replace  $\theta$  in equation (1). The solution of this problem is carried out as follows:

$$R = e^{\theta/k} \quad (2)$$

and

$$k \cdot \ln R = \theta \quad (3)$$

Substituting the above values of  $R$  and  $\theta$  in equation (3) and solving for  $k$  we find the values shown below.

$R$	$\theta$	$k$
10	30.17	13.13
15	34.50	12.78
22.5	36.00	11.58
30	36.92	10.82

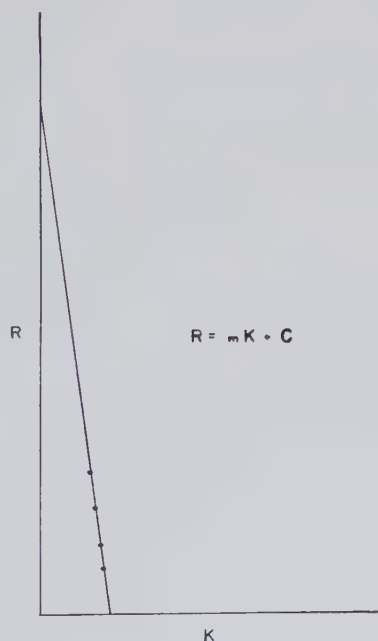


FIG. 3. Relation between  $R$  and  $K$ .

It is seen that  $k$  is a variable having an inverse relation with respect to  $R$ , and so another substitution must be made for  $k$  in order to find a more general term that can be substituted for  $\theta$  in equation (2). Continuing the empirical derivation, a plot of  $R$  versus  $k$  (Fig. 3) shows the general form

$$y = mx + c$$

where  $R$  and  $k$  are  $y$  and  $x$ , respectively, or

$$R = mk + c$$

and,

$$k = \frac{R - c}{m} \quad (4)$$

Substituting for  $k$  in equation (2) we have,

$$R = e^{m\theta/R-c}$$

$$\ln R = \frac{m\theta}{R - c}$$

and,

$$\theta = \frac{\ln R (R - c)}{m} \quad (5)$$

where,  $m=8.10$  and  $c=117.50$ .

We now have an expression for  $\theta$  in terms of  $R$  and the constants  $m$  and  $c$ . A final substitution in equation (1) gives

$$Q = \frac{A}{\tan\left(\frac{\ln R (R - c)}{m}\right)} \quad (6)$$

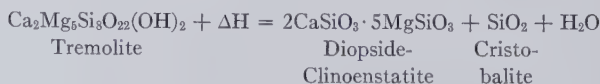
Equation (6) is the expression for calorimetric determinations with the apparatus used in this investigation. Since the derivation of the equation is empirical it is necessary to restrict its validity to the heating rates  $10^\circ \text{C}$  to  $30^\circ \text{C}$  per minute.

An examination of Fig. 1 indicates that the heating rate of  $30^\circ \text{C}$  per minute closely approaches the maximum linear heating rate for the best thermographic response with this apparatus. It is also clear that the thermographic response falls off rapidly at heating rates below  $15^\circ \text{C}$  per minute. This is an interesting characteristic in view of the fact that most investigators use a heating rate of about  $12^\circ \text{C}$ . per minute.

#### RELATION BETWEEN MASS OF SAMPLE AND THERMOGRAPHIC RESPONSE

During an investigation of the thermal properties of some amphibole minerals it became desirable to determine the optimum mass of the sample to be tested in the analyzer. The optimum mass is defined here as the minimum mass that can be employed without diminishing the accuracy of the calorimetric measurements.

Preliminary tests indicated that for the reaction<sup>3</sup>



$\Delta\text{H}$  is of the order of magnitude of 5 k.cal. per mole tremolite. Since the

<sup>3</sup> Posnjak, E., and Bowen, N. L., The role of water in tremolite: *Am. Jour. Sci.*, **22**, 203-214 (1931).

thermographic response for this reaction is in the range of 1 square inch per 100 milligrams it appeared likely that smaller samples might be thermally analyzed with no loss in the accuracy of the calorimetric measurements. A series of differential thermal analyses were then run on a random specimen of tremolite, the amounts ranging between 20 and 130 milligrams. These tests were made at a heating rate of 30° C per minute. The resulting thermographic curves describing the reaction are shown in Fig. 4 and the compiled data in Table 1. A graphic representa-

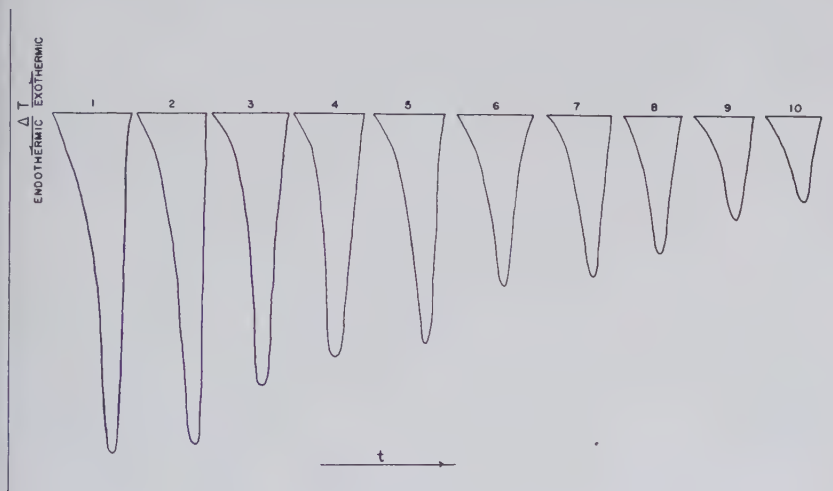


FIG. 4. Thermographic curves.

TABLE 1

Reactive Specimen (Tremolite)		Thermographic Response
Sample Number	Weight in Milligrams	Area in Square In.
1	130	1.50
2	115	1.42
3	90	1.25
4	80	1.16
5	58	0.93
6	52	0.84
7	42	0.70
8	34	0.57
9	25	0.44
10	20	0.35

tion of the data shows the relation between mass of sample and thermographic response in Fig. 5.

The plot is clearly defined and displays a marked departure from linearity when the mass exceeds approximately 60 milligrams. This loss in thermographic response is directly due to thermal gradients in the sample that become noticeably effective in samples weighing more than 60 milligrams. It should be emphasized that this relation is valid only under the conditions described here, and that other analyzers and other reactive substances might give an entirely different relation.

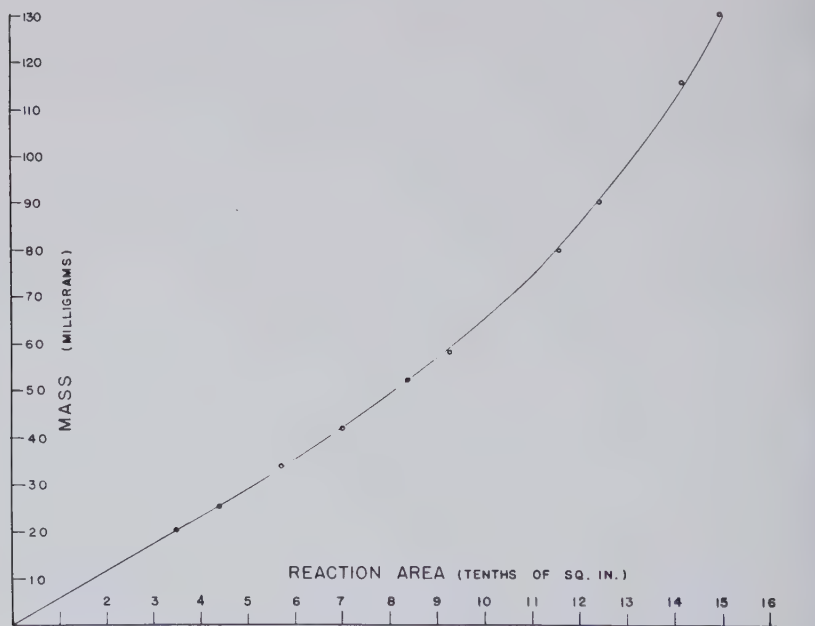


FIG. 5. Relation between mass of sample and thermographic response.

### DISCUSSION

The value of Equation (6) becomes apparent when one realizes that many chemical and physical transformations are more easily detected, and more accurately measured by differential thermal analyses at different heating rates. The chemical and physical characteristics of the particular reaction to be studied will govern the heating rate that is best suited for the investigation. Apparatus that is once calibrated can be used to make accurate calorimetric measurements without restricting the analysis to some undesirable heating rate.

The decrease in thermographic response as a result of thermal gradients



in the sample reveals the importance of a proper choice in the mass of sample to be tested. The optimum mass of sample is determined by the thermal characteristics of both the reactive sample and the analyzer apparatus. As a result they must be examined together before any accurate calorimetric measurements can be made.

Increased sensitivity of thermographic response is one of the most-sought improvements in differential thermal analysis equipment. The results of this investigation indicate that further reduction of the mass of the furnace housing would increase the sensitivity in two ways, (1) allow a wider range of heating rates to be used, and (2) permit larger samples to be tested without decreasing the accuracy of the thermographic response. Where heats of reaction are very small, say less than 0.2 cal. per gram, the second improvement would be especially useful.

*Manuscript received March 8, 1951*

## NOTES AND NEWS

### A HIGH TEMPERATURE STAGE FOR THE POLARIZING MICROSCOPE

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#### *Introduction*

In order to study polymorphic transformations in crystals at high temperatures we found it necessary to construct a microscope stage which would permit observation of crystals in crossed polarized light at carefully controlled and measured temperatures as high as 800° C.

The stage constructed for the purpose is of such simple design and has been found so satisfactory that it was thought that details of its construction might be of interest to others confronted with the same problem.

#### *Design, Materials and Construction*

Essentially the "stage" consists of a heated *metal mass* surrounded by a mass of *insulating material* with the crystals and thermocouple in the center of the hot metal mass. Figure 1 is a scale drawing of the stage and Figs. 2 and 3 show the stage, first, disassembled and, second, mounted for use.

The *metal mass* consists of two superposed right circular cylinders of INCONEL, an alloy available from the International Nickel Company, which is chemically and mechanically stable at high temperatures. Each of these has a central cylindrical hole of small diameter for the light path and a shallow cylindrical recess of larger diameter in its upper surface to accommodate a polished fused silica disc. The lower disc is the surface on which the specimen lies. The upper disc serves to reduce heat loss.

In the under surface of both pieces is an annular trench in which the coiled nichrome heating element lies, insulated from the metal cylinder by asbestos paper. Pieces cut from the heating element from an "Eagle Straight Glocoil" heater, available from the Eagle Electric Manufacturing Company, Inc., Long Island City, New York, were found to be satisfactory. The resistance of each of the pieces used was about 2 ohms. The cut ends of the heating element were allowed to extend at right angles to the axis of the cylinders for about an inch, the end being doubled back on to the standing part of the wire to decrease heating of the lead wires.

The upper metal cylinder also has in its lower surface a small straight radial trench which fits over the thermocouple housing when the stage is assembled. The chromel-alumel thermocouple, of .005" wire is led in

to the center of the stage through a double-barreled ceramic tube. It lies directly on the lower fused silica disc beside the specimen to be studied and is, therefore, in the field of view (see Fig. 4.)

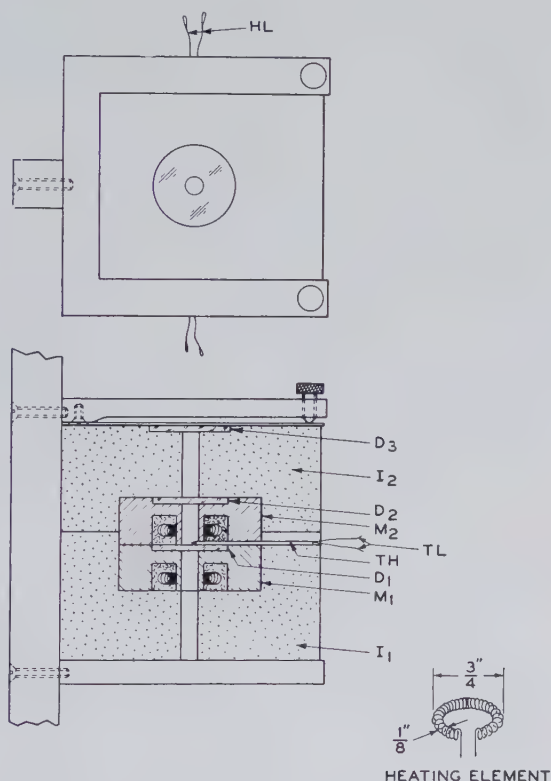


FIG. 1. Diagrammatic cross section of the heating stage

- |                              |   |
|------------------------------|---|
| $I_1$ lower insulating block | $TL$ thermocouple leads                                     |
| $I_2$ upper insulating block | $HL$ heating-element leads                                  |
| $M_1$ lower metal cylinder   | $D_1$ fused silica disc on which the specimen lies          |
| $M_2$ upper metal cylinder   | $D_2$ fused silica disc to reduce heat loss at top of $M_2$ |
| $TH$ thermocouple housing    | $D_3$ pyrex disc to reduce heat loss at top of $I_2$        |

The *insulating material* surrounding the metal mass is a pair of rectangular blocks with central cylindrical recesses to accommodate the metal cylinders. Both blocks have a small central cylindrical hole for the light path. In the top surface of the lower block, in which the lower metal cylinder rests, are five small radial trenches, two for each pair of heating element leads and one for the thermocouple housing. In the photograph in Fig. 2, the lower block is shown with the lower metal

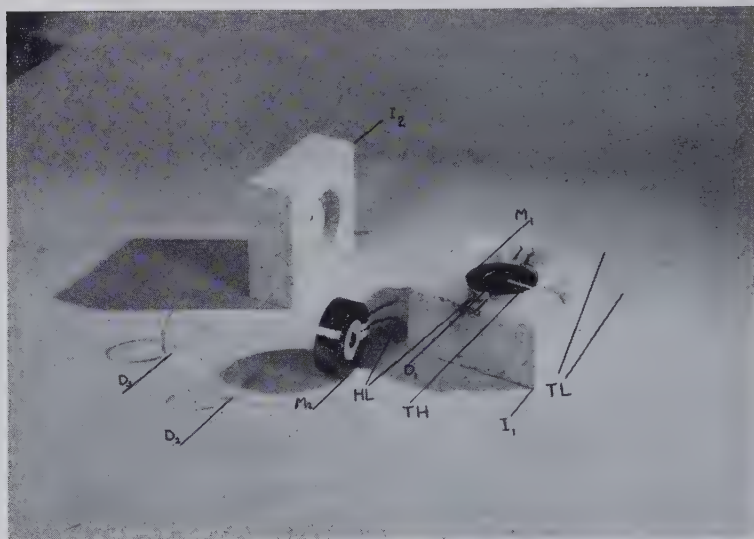


FIG. 2. Photograph of stage, partially disassembled

$I_1$  lower insulating block

$I_2$  upper insulating block

$M_1$  lower metal cylinder

$M_2$  upper metal cylinder

$TH$  thermocouple housing

$TL$  thermocouple leads

$HL$  heating-element leads

$D_1$  fused silica disc on which the specimen lies

$D_2$  fused silica disc to reduce heat loss at top of  $M_2$

$D_3$  pyrex disc to reduce heat loss at top of  $I_2$

cylinder in place, its heating element leads lying in their trenches. The thermocouple trench is at right angles to these trenches. The top insulating block which fits down over the upper metal cylinder when it has been put in place has a shallow recess in its upper surface to accommodate a pyrex disc used to reduce heat loss. The material used for these blocks was SILOCELL obtainable from Johns Manville but other insulating brick might serve as well.

The heating elements were energized through a 10 volt, 12 amp. transformer connected to a variac drawing current from the 110 volt 60 cycle line. The two heaters were connected in parallel.

### Mounting

The photograph in Fig. 3 shows the manner in which the stage was mounted for use. The simple microscope used on the brass rod mount

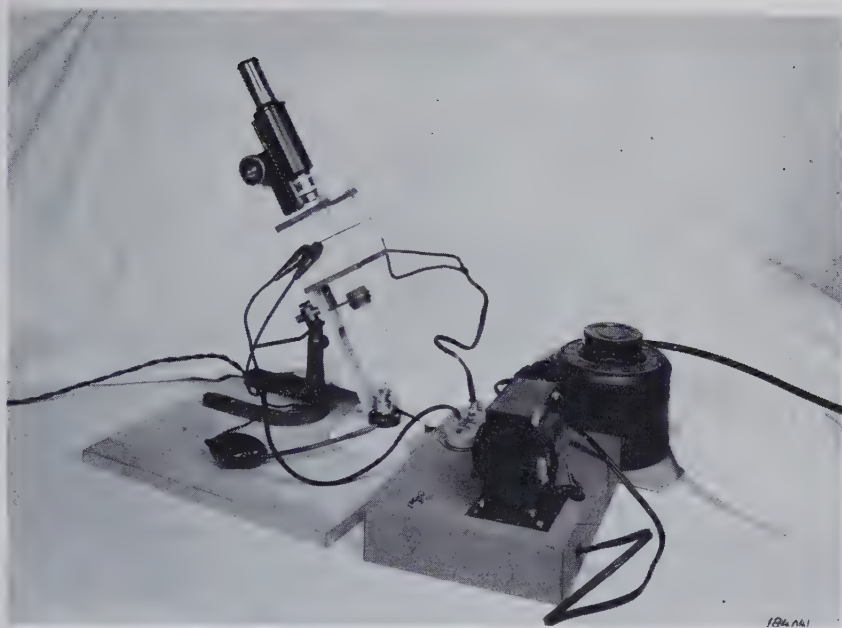


FIG. 3. Photograph of stage, mounted for use.

was one previously assembled by Mr. W. L. Bond for other purposes. The details of the spring holder designed for the heating stage are shown in the diagram in Fig. 1. A 150 watt projection lamp was used as a light source and pieces of polaroid were mounted below the stage and on top of the ocular of the microscope. The cheapest grade of polaroid was used with the expectation that it would have to be frequently discarded because of deterioration when heated. It has, however, shown no signs of deterioration after nearly 100 hours of use. The image was found to be greatly improved by the insertion of a diffusing screen between the light source and the stage. A piece of cellulose acetate with a frosted surface was used. This was mounted with the lower polaroid in a collar shown in Fig. 3 which could be easily rotated. The upper polaroid is rotated by rotating the ocular.

#### *Performance and Maintenance*

Figure 4 is a photomicrograph of sodium niobate taken with this microscope at  $560^{\circ}\text{C}$ . The lighting of the field is uniform and the image satisfactorily sharp. The fact that surrounding light does not reach the field of view is an advantage. The field of view has an area of approximately 8 square millimeters. Exploration of this area with the thermocouple showed no measurable temperature variation to exist.



Although the stage was designed for slow heating and cooling, heating rates as high as  $1^{\circ}$  per second have been used without damage to the equipment. Cooling rates are slow because of the large heat capacity of the metal mass and the low conductivity of the insulation. A typical average cooling rate is  $10^{\circ}$  per minute when the power has been turned off. The highest temperature to which the stage has been heated to date



FIG. 4. Photomicrograph of sodium niobate at  $560^{\circ}$  C. Length of crystal: 1.05 mm.

is  $800^{\circ}$  C but it could probably be heated to  $1,000^{\circ}$  C without damage to the heating elements. Prolonged heating above this temperature will result in the devitrification of the fused silica discs.

Since the parts of the stage are simply fitted together and not clamped or cemented in any way, the whole can be disassembled and reassembled in a few minutes. Thus, the crystals under observation or the heating elements, in case of burn out, can be easily replaced.

The writer is grateful to W. L. Bond for helpful advice with respect to materials used in the stage, to Mr. J. A. deFeo for its construction.

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# THE DEVELOPMENT OF TWINNING IN THE DEHYDRATION OF BRUCITE

JULIO GARRIDO, *Lagasca 123, Madrid, Spain.*

Research carried out on the structure of dehydrated brucite has shown (1), (2), (3) that the  $\text{MgO}$  crystals, formed at the expense of the  $\text{Mg}(\text{OH})_2$ , have an orientation related to that of the brucite. The  $\text{MgO}$  crystals adopt two different orientations that are as follows:

Orientation I		Orientation II	
$\text{Mg}(\text{OH})_2$	$\text{MgO}$	$\text{Mg}(\text{OH})_2$	$\text{MgO}$
$\{0001\}$	$\parallel \{111\}$	$\{0001\}$	$\parallel \{111\}$
$\{10\bar{1}0\}$	$\parallel \{011\}$	$\{10\bar{1}0\}$	$\parallel \{011\}$
$\{10\bar{1}1\} \sim \parallel$	$\{001\}$	$\{1\bar{1}01\} \sim \parallel$	$\{001\}$

The two orientations correspond to those of the two members of a spinel twin. A dehydrated crystal of brucite is an assemblage of  $\text{MgO}$  crystals with two different orientations; it is a typical case of transformation twins.

I have studied, by means of the diffraction of  $x$ -rays, the development of these twins as a function of the degree of dehydration. A crystal of brucite (from Texas) was heated at a constant temperature for a period of time, and from its loss of weight the amount of water driven off was determined. The crystal in different states of dehydration was studied by the rotating crystal method and by Weissenberg photographs. Figure 1 shows the curve of dehydration obtained at  $500^\circ \text{C}$  with a crystal of size  $3 \times 0.7 \times 0.3 \text{ mm}$ .

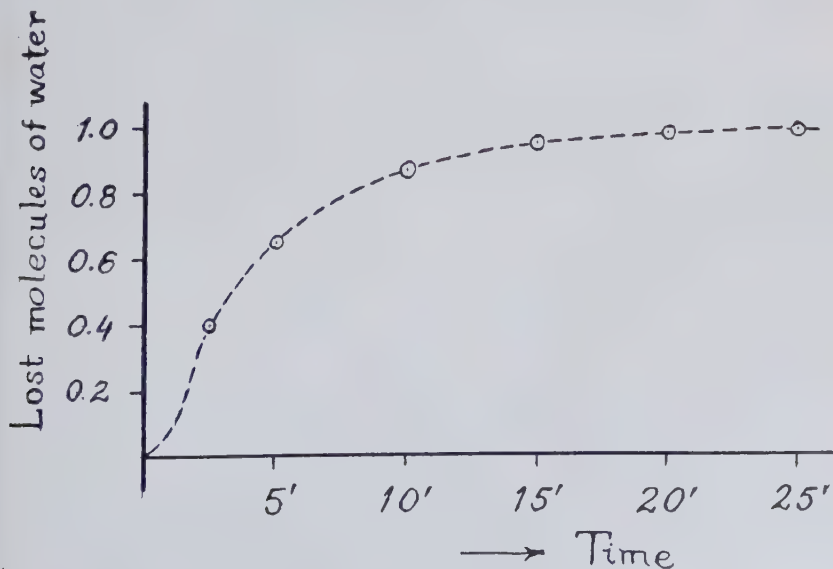


FIG. 1

On the x-ray diagrams we can easily see the reflections due to the presence of either of the phases. The reflections of the  $\text{Mg}(\text{OH})_2$  are sharp, while those of the  $\text{MgO}$  appear widened and diffuse due to the reduced size of the crystallites of the oxide. Figure 2 shows a Weissenberg photograph of a partially dehydrated crystal in which the reflections of the brucite can be seen together with those of the  $\text{MgO}$ .

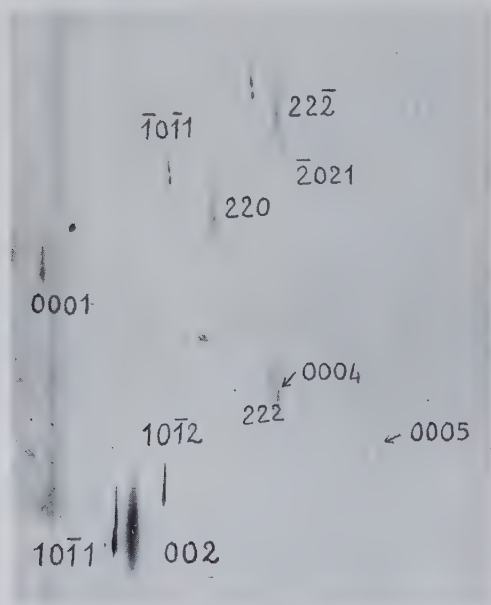


FIG. 2

When the dehydration is completed the photograph (Fig. 3) shows the reflections corresponding to the two orientations of the  $\text{MgO}$ . If we study these diagrams we may see that the reflections corresponding to orientation I are more intense than those corresponding to orientation II. There is a greater proportion of crystals that adopt orientation I.

By means of a photometric study of the reflections, the proportion of each orientation can be determined. This proportion varies between the limits of 75-80% for orientation I and 25-20% for orientation II. The diagrams obtained with crystals dehydrated progressively permit one to study the development of the crystals with the two orientations. When the amount of water given off reaches 20%, we begin to get the reflection 200 corresponding to orientation I; we can not observe the orientation II until the amount of water given off is higher than 50%. Figure 4 shows the nature of the results obtained when the crystals are dehydrated at



corresponding to orientation I can be observed; the reflections are then more sharp, probably because the crystals are larger due to recrystallization. The dominance of orientation I is undoubtedly due to the fact that in nuclei having this orientation the Mg—O bonds have the same orientation that they had in the hydroxide, while in the crystals of the second orientation the Mg—O bonds are along directions different from those the bonds had in the brucite (Fig. 5).

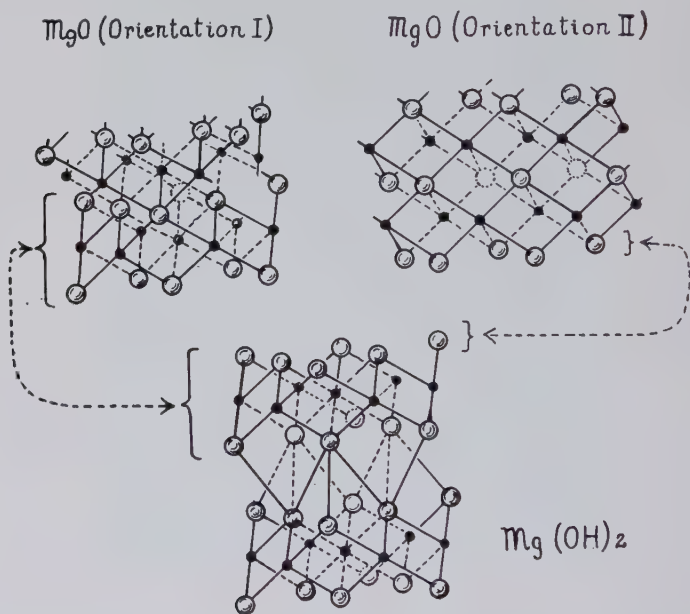


FIG. 5

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## NOTE ON THE OCCURRENCE OF CORUNDUM IN IDAHO\*

VERNE C. FRYKLUND, JR., *University of Idaho, Moscow, Idaho.*

During the field season of 1950 a corundum occurrence in sec. 22, T. 11 N., R. 4 E., of Valley County, 5 miles east of Smiths Ferry, was brought to the attention of the writer by Mr. Wayne Bowman, of Garden

\* Published by permission of the Director of the Idaho Bureau of Mines and Geology.



Valley, Idaho The occurrence was briefly visited by Mr. Bowman, the writer, and Mr. C. C. Popoff of the U. S. Bureau of Mines, in August of 1950. This occurrence is unique among known occurrences in Idaho in that the mineral lies in its original matrix; it probably represents the type of material which is the original source of the corundum found in Idaho gold placers.

Corundum has been reported from a number of gold placers in Idaho but, with one possible exception, the source rock has never been identified. It has been reported in the gold placers of Gold Fork and other tributaries of the Payette River in Boise County (Shannon, 1926, p. 193); blue and green sapphires have been reported near Pierce, in Clearwater County along Rhodes and Orofino creeks (Shannon, 1926, p. 193); as a very rare constituent of the Kelly Gulch placers at the north end of the Stanley Basin in Custer County (Stinson, 1950, p. 19); in gold placers near Resort in Idaho County (Shannon, 1926, p. 144); as a rare constituent in Salmon River gravels north of Lucile in Idaho County (Stinson, 1950, p. 28); as a common constituent in the Secesh placers south-east of Burgdorf (Stinson, 1950, p. 37); and also in the gold placers 5 miles north of Burgdorf in Idaho County.

The occurrence of corundum in the Rock Flat gold placer near Meadows, in Adams County, is of particular interest because the source of the material may have been established.

"The general formation of the district is gneiss, and the corundum crystals, which include some of gem quality, seem to be derived from a wide dike of basaltic clay formation with a peculiar spheroidal structure." (Quoted from *Mining World*, April 6, 1907, p. 449, by Mineral Resources of the United States for 1906, *U. S. Geological Survey*, 1907, p. 230.) It was suggested (Mineral Resources, 1907, p. 230) that prospecting the basalt dikes of the region might result in the discovery of more gem material. Shannon (1926, p. 193), however, said that, "the mineral has in no instance been found in its original matrix."

The corundum crystals in this new occurrence are metacrysts in schist inclusions in granodiorite of the Idaho batholith. The largest inclusion noted was thirty feet in diameter so the occurrence does not present commercial possibilities.

The corundum schist is dominantly composed of dark olive-green biotite, oligoclase (about  $An_{11}$ ) and corundum. The corundum crystals reach three centimeters in length and two centimeters in diameter, but crystals one to two millimeters long are also common. These crystals comprise from fifteen to twenty per cent of the rock. The biotite averages two to three millimeters in diameter. The feldspar, which has a tendency to concentrate around the corundum, averages 0.1 millimeters in diameter.

Minor amounts of an unidentified amphibole, chlorite, muscovite, magnetite and martite are also present, the last three as inclusions in the corundum.

No well formed corundum crystals are present, many are irregular in shape and some have an almost tabular habit. The majority of the crystals have a linear orientation in the plane of the foliation of the schist.

The color of the crystals varies from light gray to buff. Crushed fragments are mainly clear, but very pale blue, lavender, and pink fragments are also present. The specific gravity of selected material, as determined with a pycnometer is low, 3.91, as compared with the specific gravity given by Ford (1932, p. 522); but well within the range of specific gravities presented by Barlow (1915, p. 123). The indices of refraction were not accurately determined. The identity of the material was confirmed by means of an x-ray pattern, by Dr. J. W. Gruner of the University of Minnesota.

This particular area can not be considered as a potential source of corundum; however, an examination of the thin belt of metamorphic rocks on the border of the Idaho batholith, 12 miles to the west, might be of interest.

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#### DOUBLE FLUORIDES OF ZINC

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The following observations were made in connection with work on the preparation of  $\text{ZnF}_2$  and similar compounds for use as phosphors.

When  $\text{ZnO}$  or  $\text{ZnCO}_3$  is dissolved in excess HF solution, it immediately precipitates  $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ , which is biaxial, negative,  $2V$ , ca.  $50^\circ$ ,  $\alpha$ , ca. 1.46;  $\gamma$ , ca. 1.47. The product usually contains some  $\text{ZnO}$ , probably because the material never has been entirely in solution.  $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$  pre-

pared from solutions of  $\text{ZnSO}_4$  and  $\text{NaF}$  does not appear to have  $\text{ZnO}$  at first, but after decomposing to  $\text{ZnF}_2$  by heating, the product always contains  $\text{ZnO}$  formed by reaction with the water of hydration. Dehydration appears to take place in two stages, one between  $85^\circ$  and  $90^\circ \text{C}$ , the other at about  $100^\circ \text{C}$ . A satisfactory method of making  $\text{ZnF}_2$  is by heating the double salt,  $\text{NH}_4\text{F} \cdot \text{ZnF}_2$ , which is uniaxial, positive,  $\omega$ , 1.47;  $\epsilon$ , 1.481.  $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ , prepared as described above is soluble in  $\text{NH}_4\text{OH}$  solution, and impurities such as  $\text{ZnO}$  can be removed by filtration. Addition of  $\text{HF}$  precipitates the double fluoride. Most of the zinc is precipitated while the solution is still alkaline, and it is best to stop the addition of  $\text{HF}$  before the  $\text{NH}_4\text{OH}$  is completely neutralized. The crystalline precipitate is then filtered off, and the  $\text{NH}_4\text{F}$  driven off at a low heat, about  $150^\circ \text{C}$ .

Several double fluorides of the alkaline-earth metals with  $\text{ZnF}_2$  were prepared in this manner. All are uniaxial, and of low birefringence.

$\text{MgF}_2 \cdot \text{ZnF}_2$  was prepared from  $\text{MgCO}_3$  and  $\text{ZnO}$ . A mixture of these compounds, mol ratio 1:1, was covered with an excess of  $\text{HF}$  and evaporated to dryness on a hot plate, then heated at  $200^\circ \text{C}$  for an hour to drive off the excess  $\text{HF}$ . The resulting product was a very fine white powder which appeared amorphous under the microscope. Some of the powder was heated to  $1200^\circ \text{C}$  in 45 minutes and held at  $1210^\circ \text{C}$  for 5 minutes. The charge cooled to a slightly bluish, flattened boule with bladed structure. The boule contained a little  $\text{ZnO}$  and some isotropic crystals with index above 1.425, but most of it was relatively clear  $\text{MgF}_2 \cdot \text{ZnF}_2$ . This compound has a melting point of  $1185^\circ \text{C}$ ; it is uniaxial positive with  $\omega$ , ca. 1.40 and  $\epsilon$ , ca. 1.41. These low indices of refraction are surprising for they are so much nearer those of  $\text{MgF}_2$ ,  $\omega = 1.378$  and  $\epsilon = 1.350$ , than those of  $\text{ZnF}_2$ .

$\text{CaF}_2 \cdot \text{ZnF}_2$  was prepared by direct fusion of a mixture of  $\text{CaF}_2$  and  $\text{ZnF}_2$  of mol. ratio 1:1 in a graphite crucible. The product was a single crystalline phase, except for a small amount of  $\text{ZnO}$ . Its melting point is  $796^\circ \text{C}$ . This compound is uniaxial negative, with  $\omega = 1.465$  and  $\epsilon = 1.455$ .

$\text{SrF}_2 \cdot \text{ZnF}_2$  was prepared by treating a mixture of  $\text{ZnO}$  and  $\text{SrCO}_3$  with an excess of  $\text{HF}$ . The resulting powder was heated to  $950^\circ \text{C}$  for 2 hours in a graphite crucible. This compound resembles  $\text{BaF}_2 \cdot \text{ZnF}_2$  in appearance but is not quite so platy. It differs only slightly in optical properties from the calcium compound, being also uniaxial negative, mean index = 1.455. Its melting point is  $729^\circ \text{C}$ .

$\text{BaF}_2 \cdot \text{ZnF}_2$  was prepared by mixing  $\text{BaCO}_3$  and  $\text{ZnF}$  in mol. ratio 1:1 and evaporating to dryness at  $120^\circ \text{C}$  with an excess of  $\text{HF}$ . The resulting powder was heated to  $1150^\circ \text{C}$  for 20 minutes in a graphite crucible. On slow cooling the melt crystallized to a single crystalline platy (almost

micaceous) phase. The melting point of this compound is 790° C. It is uniaxial negative with a mean index of about 1.544. Its birefringence is less than that of quartz, probably near 0.004.

$\text{MnF}_2 \cdot \text{ZnF}_2$  was prepared by treating a mixture of  $\text{MnCO}_3$  and  $\text{ZnF}_2$  of the proper stoichiometric proportions with an excess of HF, evaporating to dryness and fusing the resulting powder in a graphite crucible at 1000° C. A single phase results, uniaxial positive,  $\omega = 1.487$ ,  $\epsilon = 1.517$ ; m.p. = 897° C.

A double compound,  $\text{ZnF}_2 \cdot \text{ZnCl}_2$ , was made by fusing together the two components. It melts at 685° C, is biaxial, positive,  $2V = 70^\circ$ ; mean index, ca. 1.70, birefringence less than quartz.

The properties of the compounds, the preparations of which are described above, are assembled in the accompanying table.

PROPERTIES OF  $\text{ZnF}_2$  AND RELATED COMPOUNDS

Compound	Melting Point ° C.	Optical Character	2V	$\omega$ or $\alpha$	$\epsilon$ or $\gamma$	Biref.
$\text{ZnF}_2$	872	Uniaxial+	—	1.510	1.526	.016
$\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$	d. < 100	Biaxial —	$50^\circ \pm$	1.46	1.47	.010
$\text{NH}_4\text{F} \cdot \text{ZnF}_2$	d. < 150	Uniaxial+	—	1.47	1.481	.011
$\text{MgF}_2 \cdot \text{ZnF}_2$	1185	Uniaxial+	—	1.40	1.41	.010
$\text{CaF}_2 \cdot \text{ZnF}_2$	796	Uniaxial—	—	1.465	1.455	.010
$\text{SrF}_2 \cdot \text{ZnF}_2$	729	Uniaxial—	—	mean index	1.455	< .009
$\text{BaF}_2 \cdot \text{ZnF}_2$	790	Uniaxial—	—	mean index	1.544	.004 $\pm$
$\text{MnF}_2 \cdot \text{ZnF}_2$	897	Uniaxial+	—	1.487	1.517	.030
$\text{ZnF}_2 \cdot \text{ZnCl}_2$	689	Biaxial +	$70^\circ \pm$	mean index	1.70	< .009

#### DETECTION OF FLUORITE IN SANDS WITH ZIRCONIUM-ALIZARIN SOLUTION

ROBERT M. GROGAN, *Illinois State Geological Survey*.\*

The presence of grains of fluorite in natural sands or other assemblages of loose mineral fragments may be readily detected with the aid of a zirconium-alizarin test solution described by Feigl.<sup>1</sup> The technique described here was adapted and used recently in the examination of soil samples taken from above known or suspected fluorspar veins in the fluorspar mining district of southern Illinois. The purpose of this study

\* Published by permission of the Chief, Illinois State Geological Survey, Urbana, Illinois. Since May 1, 1951 the author has been employed as Geologist, Development Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware.

<sup>1</sup> Feigl, Fritz (1937), Qualitative analysis by spot tests, 161-163.

was to test the thesis that concealed veins might be discovered or the course of known veins traced by means of grains of fluorite in the soil which would thus be an aid to prospecting.

Portions of the soil samples are soaked in water, dispersed in a mechanical stirrer with the aid of a little sodium silicate defloculant, and wet-sieved over a 200 mesh screen. After drying, the fraction coarser than 20 mesh is removed by sieving, and the remainder separated into light and heavy fractions with bromoform. The heavy fraction is then freed of most of its content of limonitic pellets with an electromagnet and then tested for fluorite. This is accomplished by spreading the grains thinly and evenly over the surface of Whatman No. 1 filter papers 9.0 centimeters in diameter which have been dipped in zirconium-alizarin solution and suspended within watch glasses 10.0 centimeters in diameter in such manner that only the edge of the paper makes contact with the glass. The solution imparts a deep red-violet color to the papers. Yellow spots appearing after an interval of 10 to 20 minutes indicate the presence and location of fluorite grains. Often the yellow spots can be best seen by holding the watch glass up to a light and viewing the test paper from the underside. Larger watch glasses inverted over the ones supporting the filter papers prevent the latter from drying too quickly.

The zirconium-alizarin solution is made as recommended by Feigl; 0.05 g. of zirconium nitrate is dissolved in 50 cc. of water and 10 cc. of concentrated hydrochloric acid, and mixed with a solution of 0.05 g. of sodium alizarin sulfonate (Alizarine Red S) in 50 cc. of water. This solution is quite stable. Fluorite grains in contact with the solution are partially dissolved, with the result that the colorless complex ion  $(\text{ZrF}_6)^-$  is formed and alizarin, a yellow dye, is liberated in the immediate vicinity of the grains.

The only interfering substances encountered in the recent studies were iron compounds, mostly in the form of limonite pellets, and fragments of a material of unknown composition which softened and disintegrated on exposure to the test solution. The limonite is slowly attacked by the hydrochloric acid and the resulting iron chloride stains the paper yellow, an effect noted principally when the paper dries. The fragments of unknown composition reacted with the solution faster than fluorite and produced white spots rather than yellow ones. Sulfate ion interferes with the test if it is in solution, but preliminary tests showed that barite, the only sulfate apt to occur in the soil samples studied, did not dissolve and react with the zirconium-alizarin solution. In applying the test to new materials it would be advisable to check results with the microscope until the operator was able to distinguish between spots produced by fluorite and by interfering substances.



The technique as used so far was designed to be only roughly quantitative. Roughly equal volumes of the heavy fractions were used each time and a record kept of the number of fluorite grains noted. By using weighed amounts of material more exact determinations of fluorite content could be made. Experiments with artificial mixtures of fluorite and quartz sand showed that as little as 0.1% of fluorite could be easily detected.

The zirconium-alizarin technique was developed to supplant the microscopic methods formerly used for detecting fluorite. It is a routine operation which can be done by personnel not trained in the use of the microscope, it consumes less time and is probably more accurate on low-fluorite samples than the microscope method.

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FIRST INTERNATIONAL CONVENTION OF MINERAL RESOURCES

*Mexico City, October 29 to November 4, 1951*

The Mineralogical Society of America has accepted an invitation to participate in this convention and it is hoped that many Fellows and Members of the Society will make an effort to be present.

The convention will consist of the following meetings to be held concurrently:

FIRST NATIONAL CONGRESS OF MINERAL RESOURCES

GENERAL MEETING NO. 172 OF THE AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

THIRD CONGRESS OF THE PANAMERICAN INSTITUTE OF MINING ENGINEERING AND GEOLOGY

For further information address Ing. Raúl de la Peña, Director General, Instituto Nacional para la Investigacion de Recursos Minerales, Av. Morelos No. 110, Desp. 207, México 1, D. F., México.

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The first issue of the *Journal of Geological Education*, published by the Association of Geology Teachers, appeared in April 1951. Volume 1, No. 1 is devoted to teaching methods in mineralogy. Nine short articles comprise the Contents as follows: Geological Mineralogy by C. J. Roy; Mineralogy for Embryonic Professional Geologists by D. Jerome Fisher; An Outline of a Course in Elementary Mineralogy by Cornelius S. Hurlbut, Jr.; Automatic Testing Program in Mineralogy by A. C. Swinnerton; Teaching Procedure in Undergraduate Mineralogy Courses by Kiril Spiroff; Crystallography in the General Mineralogy Course by Brian Mason; Mineralogy and Crystallography in Engineering Curricula by Oliver R. Grawe; Binocular Microscope Studies in the Teaching of Mineralogy and Petrology by R. W. Edmund; and Cleaning Mineral Specimens by David E. Jensen.

The *Journal of Geological Education* is published semiannually by the Association of Geology Teachers. The annual subscription price is \$2.00. Single issues are \$1.15. The officers for 1950-51 are:

President—Paul R. Shaffer (University of Illinois).

Vice-President—Rudolph W. Edmund (Augustana College).

Secretary-Treasurer—Raymond C. Gutschik (University of Notre Dame).

Editor—William F. Read (Lawrence College).

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Heinrich Ries, professor emeritus of economic geology, Cornell University, died April 11 at Ithaca, New York, at the age of seventy-nine years.

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To correct some errors which have been discovered in the fourth edition of Part II of Winchell's Elements of Optical Mineralogy an errata sheet is now available by request from the publishers, John Wiley and Sons, of New York.

#### MINERALOGICAL SOCIETY (LONDON)

A meeting of the Society was held on Thursday, June 7, 1951, in the apartments of the Geological Society of London, Burlington House, Piccadilly, W.1 (by kind permission).

The following papers were read:

- (1) A new beryllium mineral, discovered as a gem-stone.

By Mr. B. W. Anderson, Mr. C. J. Payne and Dr. G. F. Claringbull, with a microchemical analysis by Dr. M. H. Hey.

This pale-mauve transparent mineral at present known only as two faceted gemstones is hexagonal with  $a=5.72 \text{ \AA}$  and  $c=18.38 \text{ \AA}$ ; space group  $D_6^h=C6_2$ . Refractive indices  $\omega=1.723$  (1.721),  $\epsilon=1.719$  (1.717); density 3.62 (3.59). Microchemical analysis gives the composition  $\text{Be}_4\text{Mg}_4\text{Al}_6\text{O}_{32}$ .

- (2) The amygdale minerals in the Tertiary lavas of Ireland. (1) The distribution of chabazite habits and zeolites in the Garron plateau area, Co. Antrim.

By Mr. G. P. L. Walker.

It has been found possible to arrange chabazite habits in a habit series ranging from the simple, untwinned unit rhombohedron to the complex-twinned varieties, phacolite and herschelite. A habit notation is proposed, and a habit distribution map, perhaps the first of its kind to appear, has been prepared of seventy square miles of basalt lavas in the Garron plateau area in the east of Co. Antrim, accompanied by a section. The distribution is so regular that the habit seems to have been controlled by the temperature. The Chabazite habits fall into a number of well-defined zones superimposed upon, and therefore later than the lavas, but clearly shifted by several faults. The zeolites associated with the chabazite are described and their distribution considered. Analcime, which falls into a zone towards the base of the lavas appears, unlike the chabazite, to post-date the faulting. It is therefore possible to establish a relative chronology of events following the eruption of the lavas. Regarding the origin of the zeolites, the distribution of chabazite habits and analcime appears to support the idea which is put forward that, once initiated, the reactions resulting in the hydration of the pyrogenetic minerals in the basalts to zeolites and chlorites are capable of generating sufficient heat to maintain these reactions.

- (3) Notes on the copper deposits of Middleton Tyas and Richmond.

By Mr. M. T. Deans.

These deposits, worked mainly in the eighteenth century, occur as flats, pockets and thin veins in the Carboniferous Limestone not far below the former surface on which Permian rocks rested. Chalcocite predominates in the east, chalcopyrite in the west, and covellite and bornite are well developed, together with malachite, azurite and a little native copper. Replacements among the copper minerals are described, also chalcocite

replacing galena. Gangue minerals are absent or very subordinate, consisting of calcite, baryte and witherite, as in the nearest Pennine lead deposits. The origin of the deposits is discussed.

- (4) Cataclastic pegmatites and calc-silicate skarns near Bunbeg, Co. Donegal.

By Mr. E. H. T. Whitten.

Description is given of the Dalradian calc-silicate hornfelses and three cataclastic zoned diopside-rich pegmatites intruded into them; these dykes have produced interesting skarns. The petrogenesis of the dykes and skarns is discussed.

The following paper was taken as read:

- (1) On the occurrence of conichalcite and other minerals new and rare to Britain.

By Mr. A. W. G. Kingsbury and Mr. J. Hartley.

New and recent occurrences of conichalcite in Devon, antlerite and cyanotrichite in Cornwall, carminite in Cornwall and Cumberland, and zeunerite, plumbogummite and other minerals in Cornwall are described.

*(Titles and abstracts kindly submitted by G. F. Claringbull, General Secretary)*

## BOOK REVIEWS

SILICATE MELT EQUILIBRIA. By WILHELM EITEL, x+159 pp., 200 figs. New Brunswick, New Jersey, Rutgers University Press, 1951. \$5.00.

This little book is a translation from the German *Die heterogenen Schmelzgleichgewichte silikatischer Mehrstoffsysteme*, first published in 1943. Of the first edition only a single copy survived the bombing of Leipzig in 1944. A second printing was made in 1945, but of this only the author's copy appears to be available in this country. Translation was carried out principally by J. G. Phillips of the Department of Mines and Resources, Ottawa, Canada, and his late colleague, T. G. Madgwick. They had the advice and assistance of a committee of the American Ceramic Society under the chairmanship of R. B. Sosman. Unfortunately, these collaborators have not always translated the German all the way to English. The corners of a triangle are, in at least one place, referred to as its end points and even the eagle eye of Sosman did not catch the sentence, "From F. A. H. Schreinemakers' detailed theoretical work on three-component systems of this kind, only so much is here extracted, for example that which concerns ternary silicate-systems in equilibrium with sulphide or oxide melts."

This reviewer does not share the translators' aversion to the use of the straightforward translation of the German, "feste Lösungen," namely, "solid solutions." Those who work with them most call them just that almost invariably. Occasionally they speak of mix-crystals, to which the translators object also, but their objection is not well taken. It would apply only to the expression "mixed crystals," which has a possible significance in everyday parlance, but "mix-crystals" is a purely technical term without possible ambiguity. In adopting the term "crystalline solutions" the translators have only added to the language burden, though the expression is in itself irreproachable.

The book presents a graded series of equilibrium diagrams of systems of more than one component with a discussion of them. Such material, brought together in English, will prove very useful to a great number of technologists and petrologists.

Beginning with a statement of the phase rule, which is the principle governing all aspects of these diagrams, the author leads the reader from the more simple binary diagrams into those involving phase transformations, to others involving solid solutions, immiscibility in the liquid state and all the well-known complications of binary systems. From these one passes to the simpler diagrams of ternary systems, then to those involving the same complications and finally comes to equilibria in multi-component systems. All of this is presented in the conventional manner, as developed principally by the Dutch masters of heterogeneous equilibrium, but emphasis is laid on those types of diagrams that are most likely to be encountered in silicate systems. Most of the diagrams are theoretical but a few are of actual investigated systems.

The author states frankly in the preface that he has not attempted to give exhaustive references. There are, however, 92 in all, which is a considerable number for a small book, and one cannot fail to wonder whether a more judicious choice might not have been made. Many refer to papers treating the particular question under discussion in a theoretical manner, a type of treatment of practically all the questions to be found brought together in one place in the larger treatises. Probably a greater proportion of references to experimentally determined examples, illustrating the principles involved, would have led to greater usefulness. For example, in discussing liquid immiscibility in binary and again in ternary systems, the author mentions the actual systems in which the phenomenon has been observed but the papers detailing the investigations are not referred to and the name of Greig, who carried out all of the investigations on these systems, is not mentioned.

The above general suggestion is made in the interest of greater usefulness of a possible

second edition and there are a few matters of detail that may be mentioned with the same end in view.

As has already been said the book begins with a statement of the phase rule, which requires that for invariancy the number of phases must exceed the number of components by two. For the novice it would have been well if the author had made it clear why it is that in silicate diagrams a number of phases exceeding the number of components by only one is ordinarily regarded as giving invariancy. It is, of course, because the vapor phase in such systems can be neglected and pressure is not ordinarily to be considered as a variable. The importance of keeping these facts in mind is realized when one finds that the author himself has not always done so. Thus in figure 6, where the effect of the pressure variable is definitely under consideration, the author depicts, in the curve  $ue_2'$ , the change from incongruent to congruent melting induced by pressure and says that, in the special limiting case shown in the separate diagram figure 7, there is a four-phase point at which crystal phases  $A$  and  $A_mB_n$  and the liquid and vapor phases coexist. Actually the special point is like any other point in  $ue_2'$ , namely one at which said two crystal phases are in equilibrium with liquid in the absence of vapor. The vapor phase can exist along this univariant curve only at the invariant (quadruple) point (at some very low pressure less than  $p_1$ ) at which the curve, as well as three other curves, originates. The only special features of the limiting case depicted in figure 7 is that the liquid phase happens to have the composition of the compound  $A_mB_n$ . Moreover the diagram (figure 7) should be changed left for right, leaving the lettering unchanged, in order that it may properly depict a special case of figure 6.

These considerations emphasize the importance of realizing that in silicate diagrams we ordinarily neglect the vapor phase and pressure as a variable, but as soon as we begin to regard pressure as a variable we must have carefully in mind the limitations as to presence or absence of the vapor phase in order that the phase rule be properly applied.

One may question the advisability of the use of "*unstable crystal phases*" to designate stable phases existing under metastable conditions as is done in the discussion of figures 12-15.

The author states in paragraph 78 that the curves separating fields in ternary diagrams should be called "boundary curves" and that the term "eutectic curves" is less to be recommended. This reviewer agrees most heartily and is therefore somewhat disappointed to find the author using the latter in paragraph 149. The term "eutectic" should be applied only to points, never to curves.

For the novice it might have been well if the author had made it clearer that the temperature  $t_2$  of figure 16 and the temperature  $T_m$  of figure 68 are identical, provided that  $A$  and  $B$  are the same substances in both figures and no matter what the third substance  $C$  may be. A similar relation holds between figures 17 and 69.

In paragraph 162 the statement is made that  $1042^\circ$  is a temperature-minimum for the existence of leucite, according to figure 59. Understanding reference to this figure makes it entirely clear that the temperature  $1042^\circ$  is merely the minimum temperature of existence of leucite *in contact with liquid in the ternary system*, nevertheless it would have been well if the author had added the qualifying phrases here given in italics. The petrologic novice might get the impression that leucite could form only above  $1042^\circ$ , a relation which exists, without qualification of any kind, only for a compound of the type depicted in figure 68.

The new figure 124 differs from the corresponding figure 120 of the German edition in that the latter is the diagram of Ferguson and Merwin and the new figure is intended to embody corrections by Osborn. Actually one major Osborn correction is not shown, for he found that each of the curves 13-14 and 3-1 has a maximum temperature on the diopside-wollastonite join whereas figure 124 shows the temperature falling in one direction from end to end of these curves.



In paragraph 203 the author discusses the case of unmixing of solid solutions in a ternary system and correctly states that a succession of three-phase triangles develops in ternary compositions below the critical temperature of unmixing  $t_k$ . However the diagram (figure 135) which is intended to illustrate this relation is bound to give the reader an erroneous concept of the nature of these three-phase triangles. Even at the lowest temperature  $E_t$  the liquid apex  $E_t$  of the three-phase triangle should be joined to points near  $A$  and near  $B$  and not to  $A$  and  $B$  themselves. At higher temperatures successive points on the curve  $E_t t_k$  should be joined to points in  $AB$  that continually approach each other, until finally at the temperature  $t_k$  the two points should coincide and the three-phase triangle is reduced to a line. The joins  $t_k A$  and  $t_k B$  of figure 135 are thus altogether misleading.

In paragraph 205 it is stated that figure 141 is derived from figure 138, if the maximum  $K$  is shifted further into the interior of the concentration triangle. Actually no amount of movement of the maximum  $K$  can alter the fact that figures 138 and 141 are essentially different in that figure 138 shows immiscibility on the binary side-line.

The sections on four and more components summarize the various attempts that have been made to depict such systems graphically and to treat them analytically. They serve to emphasize how limited has been our progress in these directions.

As a whole the subject matter of the book is presented in a clear and orderly manner and, in spite of the few suggestions made as to corrections, the book must be regarded as an excellent addition to the literature of silicate equilibrium. It presents a large volume of facts and of the principles governing them in conveniently small compass. Most petrologists and silicate technologists will find it a desirable addition to their libraries if they can find the necessary \$5.00, which must be regarded as rather a high price for a small book. But such are the ways of university presses.

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CRYSTAL GROWTH by H. E. BUCKLEY. xv+571 pages, John Wiley and Sons, Inc., New York, New York; Chapman and Hall Ltd., London, England, 1951. Price, \$9.00.

This book is a much more complete, systematic, and comprehensive treatment than the volume of the same title published by the Faraday Society in 1949. The earlier volume is a general discussion, composed of 49 individual papers. More details of some processes are given in the Faraday volume, of course, but there are also some overlaps and some gaps not found in the integrated treatment by Buckley. In a work of such broad scope one would not expect to find experimental details of all of the processes outlined. In the preface Buckley says, "It is hoped, however, that even such [the specialists] may derive a little profit or inspiration from contact with the larger whole—and will look with tolerance on the elementary descriptions of their main preoccupations." The excellent bibliographies that follow each chapter give ample reference to original work so that anyone interested in duplicating, or extending, an experiment can find all of the pertinent details that have been published.

Perusal of the chapter headings gives the impression that the work is largely theoretical, but in most of the chapters enough specific examples are cited to give a practical turn to the theory. The titles of the chapters are: 1. Solution and solubility, solubility and super-solubility; 2. The artificial preparation of crystals; 3. The Curie theory of crystal growth; 4. The so-called velocities of growth; 5. The diffusion theories; 6. Recent theories of crystal growth; 7. Ideal and real crystals; 8. Miscellaneous types of crystallization; 9. Dissolution phenomena; 10. Crystal habit modification by impurities; 11. Relationship of substances during crystallization; 12. Peculiarities of crystal growth.

These twelve chapters form the bulk of the text and occupy 528 pages. There follows a

31-page appendix on Habit Modification as a Result of the Presence of Impurities. This is a subject in which Buckley is particularly interested and in which he has done a great deal of work. The appendix is really supplementary to Chapter 10 and in it 56 compounds are listed and variations in their crystal habit and appearance brought about by deliberate addition of impurity to the mother liquor are outlined. All of these examples are well-attested; many more were omitted where the emphasis was on systematic inclusion of the impurity and where otherwise little information was given regarding modification of habit.

At the end of the appendix there is a table in which 33 "useful habit-modifying dyes" are listed. Many other dyes mentioned in the appendix and throughout the text are not listed in the table and there is no summary of other organic modifiers such as dextrin, gum arabic, metanilic acid, and sulfanilic acid, or inorganic modifiers such as borax, metallic chlorides, and sodium sulfate, a considerable number of which are mentioned throughout the work.

Neither are these compounds listed in the index, nor are most of the compounds whose habit modifications are discussed. For example, the modification of the crystal habit of sodium chloride by urea is mentioned in at least two different places, yet neither compound is in the index. In fact, the subject index is quite a disappointment after one reads through the very complete treatment in the text. It occupies but 5 pages and only a fraction of the topics, compounds, theories, types of equipment, etc., discussed in the text are listed. The six-page author index is much more nearly complete.

Buckley has done an excellent job of summarizing existing experimental data and theories of this interesting and important field. After one reads through chapters and chapters on crystal growth and one on dissolution of crystals, however, he is impressed by how little is really *known* about why or how crystals form or dissolve.

It is surprising in a volume by one who has long been interested in mineralogy to find so little mention of natural crystals. There are many places where principles developed, or phenomena observed in the laboratory, could be applied to problems of crystallization in Nature, yet only rarely is such application attempted. For example, in the chapter on velocities of growth such factors as composition of the solution (including impurities), imperfections and orientation of the lattice, and mechanical inhibition, are discussed, but no mention is made of direction of motion of solution past a growing crystal. This factor can produce asymmetric growth on different faces of a given crystal form and thus affords an important clue in certain mineralogical and geological problems. This effect has been observed and recorded in growth of artificial crystals. Some of the references that are made to natural phenomena are antiquated if not actually in error. For example, on page 257 the terms "eutectic ground mass" and "eutectic texture" are used in discussing rocks. It has long since been demonstrated that few, if any, of the graphic textures observed in pegmatites and the groundmass of porphyries are due to crystallization at a eutectic. On the same page in a discussion of the effect of water on crystallization of a magma, a 1922 paper by Morey is quoted to the effect that "a 0.1% proportion of water will reduce the melting point of anorthite by 5° C." There has been in the literature for quite some time now much more detailed and pertinent work on the effect of water on the crystallization of silicates, some of which could have been quoted to advantage in this discussion. This lack of attention to natural phenomena is unfortunate for mineralogists, petrologists, and geologists because it renders the volume less attractive and useful to them than it might otherwise have been.

In the discussion of melting point determination on pages 260-262 considerable emphasis is laid on the difficulties brought about in the cooling or heating curve method by the tendency of many substances to undercool or superheat. Yet no mention is made of the quenching technique by which these difficulties were overcome for silicates and similar compounds many years ago at the Geophysical Laboratory.

Typographical errors are relatively few and unimportant. On page 83, line 2, "Fig. 32 *b*" should read "Fig. 32 *c*." In Fig. 34, page 85, an inlet and outlet for "CO<sub>2</sub>" are shown, but the coolant mentioned in the discussion of the figure on page 84 is "nitrogen." At the top of page 107 "and" is used in a French quotation. In the second sentence of paragraph 2, page 264, failure to close the parenthesis at the proper place, after the word "type," is confusing. The columns of Table 15*a* on page 267 should be headed "cm per min" instead of "cm per mm." Plate 59 on page 429 is a reproduction of part of plate 39 on page 363 at twice the scale, but both are marked "X2." On page 475, paragraph 2, line 6, "interfacial" should read "interfacial." Use of the term "four faced cube" on page 123 and in Fig. 51*c*, page 137, can hardly be called a typographical error, but the equivalent term "tetrahexahedron" would have been much more readily understood by (at least American) mineralogists and crystallographers.

This book is, of course, the most complete and up-to-date summary of the theory and practice of crystal growth. It is a worthy companion to the 1949 volume of the Faraday Society; both should be in the library of any individual or institution interested in any phase of the growth of crystals.

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EINFÜHRUNG IN DIE MINERALOGIE (KRISTALLOGRAPHIE UND PETROLOGIE) by CARL W. CORRENS. viii + 414 pages; 405 illustrations, 13.5 cm. Wulff net; 68 tables in Parts I and II; Part III is composed entirely of tables. Price, Bound 41.60 DM. Springer Verlag, Berlin, Heidelberg, 1949.

Professor Correns has prepared this text as an introduction to mineralogy for students in mineralogy and particularly for students in the related professions. The material was selected to meet the course requirements in German Universities. Professor Correns stresses the relationship of mineralogy to other sciences. He writes, "Other important boundary fields besides those already mentioned (mathematics and physics) are chemistry and physical chemistry and even biology in sedimentary petrology. In the life of the natural sciences, mineralogy thus stands in the midst in continuous reciprocal relation with its neighbors." This book, he feels, will lead to a comprehension of mineralogy but it will not replace a systematic textbook.

An examination of the table of contents of this book causes one to turn back and look at the title. Part I is crystallography, Part II petrology, and Part III a supplement or appendix (Anhang). Mineralogy does not appear as a heading in the table of contents.

This book is a refreshing treatment of mineralogy, using that term in its widest sense. It is original in plan, in ideas, in manner of presentation and in illustrations. In general, it is above the level of undergraduate students of mineralogy in most American universities. It should be carefully read by graduate students in mineralogy, petrology, and "hard rock" geology. Mineralogists, crystallographers, and petrologists will find this book to be well worth the effort required to read a book in a foreign language. It is both comprehensive and stimulating.

PART I: KRISTALLOGRAPHIE: *Kristallmathematik* is covered in 45 pages. Of this, 25 pages are devoted to a discussion of the 32 crystal classes and 17 pages to a discussion of the general principles of crystallography, symmetry relationships, and calculations. *Kristallchemie* occupies 40 pages in the text. This section is a brief introduction to the theory of crystal chemistry. It follows the Goldschmidt approach. Various types of binding, ionic, intermolecular, metallic, etc., are illustrated. The structure of the silicates is given in more detail than that of other substances. This section is well illustrated and contains the electron density maps of halite, quartz, diamond, and hexamethylenetetramine deter-

mined by Brill, Grimm, Hermann, and Peters. *Kristallphysik* is covered in 52 pages. This section opens with a good discussion of the plastic deformation, mechanical properties, and elastic behavior of crystals. The relationships to crystal structure are emphasized. Tabular summaries of the physical data are included. Crystal optics is covered very briefly in 22 pages. The treatment is advanced and contains discussions of strain-birefringence and form double refraction. The description of x-ray optics is also very brief. *Kristallwachstum und -auflösung*: The subject of crystal growth and solution is a relative newcomer to textbooks of mineralogy. Professor Correns has presented a very interesting introduction to this field. The data of Spangenberg on the growth of potash alum crystals, solution phenomena, and etch-figures afford the experimental background. The treatment of crystal growth in terms of lattice energy considerations follows Kossel and Stranski.

The treatment throughout Part I is brief, but should the reader gain the idea that this is all that the student need to learn, Professor Correns warns as follows:

"Wir haben mit diesen Betrachtungen die kristallographische Formenlehre abgeschlossen, ein Gebiet, das dem Anfänger besondere Schwierigkeiten zu machen pflegt. Bei vielen Menschen ist das *Raumvorstellungsvermögen* nur schwach entwickelt. Wer sich aber mit der Architektur der festen Stoffe, mit der Kristallbaukunde, beschäftigen will, muss das Raumvorstellungsvermögen entwickeln. Das geschieht durch Übung, vor allem an kleinen Holzmodellen. Das sog. Klötzchenpraktikum hat darin seinen Sinn, dass man lernt, Symmetrieelemente zu finden und zusammengehörende Flächen zu erkennen. Über diese Schulung hinaus ist aber die Kenntnis der 32 Kristallklassen und der bei ihnen vorkommenden Formen die Grundlage für die Beschreibung der Minerale, für die Untersuchung des Wachstums, der physikalischen Vorgänge, wie z. B. des mechanischen und optischen Verhaltens. Die Ansicht, dass es genüge, "ein wenig über die Struktur" zu wissen, dass aber die Kristallmorphologie "unnötig" sei, verhindert ein tieferes Eindringen in die Probleme. Auch für das Verständnis der Strukturen ist die Kenntnis der Kristallklassen Voraussetzung."

PART II: PETROLOGIE: *Einige physikalisch-chemische Grundlagen*. This section is chiefly a short description of one, two, and three component systems. The diagram for the system leucite-silica is in error and appears to be based on a mixture of old and new data on leucite. Photomicrographs and sketches are used to illustrate practical applications of the principles discussed. Under the title, "*Die magmatische Gesteinsbildung*," Professor Correns treats the fundamental processes of the origin of igneous rocks, their classifications, and Niggli numbers. He also discusses the frequency of the chemical elements, rôle of volatile constituents, critical phenomena, pneumatolysis, hydrothermal solutions, ore deposits, and the deposition of minerals in cavities in igneous rocks. This section is well substantiated by tables. The next two sections in Part II, *Verwitterung und Mineralbildung im Boden* and *Die sedimentäre Gesteinsbildung* represent Professor Correns' field of specialization and they are exceptionally well done. The approach is from the physico-chemical view. These sections are rich in original ideas and methods of presentation. The last section is closed by a discussion of the rare and unusual elements in biogenetic and chemical sediments. *Die metamorphe gesteinsbildung* is discussed in 27 pages. It includes the topics, recrystallization, deformation of rock, the facies concept, and granitization. The final section in Part II is entitled *Geochemische Ergänzungen* and contains a discussion of the concept of geochemistry, geochemical balance, and the frequency of occurrence of the chemical elements.

PART III: ANHANG: is made up of tables. This includes a tabular review of the data of the 32 crystal classes; a table showing the relationship of the Naumann and Miller indices; the symbols of the 230 space groups, expressed in Schoenflies and Hermann-Mauguin symbols; relation of crystal symmetry and physical properties; atomic and ionic radii; tabular summary of 300 common minerals and their properties. Thirteen pages of



tables are devoted to petrologic data, including average chemical analyses of rocks and modes. The book contains a collection of suitable references and it is well indexed.

The text is designed in such a way that a college professor can select those topics which he wishes to cover in a given course. He will have to expand the discussions of most topics. The tables and illustrations will prove very valuable in this connection. The tabular summary of the properties of 300 minerals is a compact presentation of the data commonly appearing as separate entities in the usual mineralogical textbooks.

The reviewer believes that Professor Correns is to be congratulated on a very fine book.

GEORGE T. FAUST

DICCIONARIO MINERO-METALÚRGICO-GEOLÓGICO-MINERALÓGICO-PETROGRÁFICO, Y DE PETRÓLEO (INGLÉS-ESPAÑOL, FRANCÉS, ALEMÁN, RUSO), by ALEJANDRO NOVITZKY, vi+369 pp. quarto, Buenos Aires, 1951.

The author is well qualified to compile a polylingual dictionary, because he was born and reared in Russia and has studied and worked in France, Germany, Yugoslavia, Turkey, North Africa, the Balkans, and Argentina. He is a mining engineer, so it is natural that this field and metallurgy should be named first and covered more thoroughly than are the related Earth Sciences.

The work contains approximately 18,000 terms, many of which are not to be found in more general technical dictionaries. It should therefore be very useful in translating from English to Spanish, French, German, or Russian, since the arrangement is alphabetical in English. For other purposes, however, it appears that its usefulness will be largely limited to checking meanings. For example, if one wishes to know the meaning of a Russian word, there is no way to look it up directly. If he has an indication of what the word means in English he can look up the English word(s) that might have the same meaning and see whether the Russian word is listed. It is unfortunate that no glossary, or index, of Spanish, French, German, and Russian terms was prepared, which would have multiplied the usefulness of the book almost fivefold. There is no indication in the introduction, or in the arrangement of the terms on the pages, that any such supplementary glossary is contemplated. It would appear that the glossary would be more than worth the extra time and expense of preparing it.

A "technical vocabulary"<sup>1</sup> published in Finland in 1950 uses this system. The words are listed alphabetically in German; on each page the lines are numbered. The index has Finnish, Swedish, English, and Russian words listed alphabetically, with reference to the proper page and line for each. This means that the book can be used for looking up the meaning of words in any of the five languages and hence for translating from any one of them to any other.

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<sup>1</sup> "Tekniikan Sanasto (Technical Vocabulary; German-English-Finnish-Swedish-Russian), xxiv+1518 pp. (exclusive of index, which is a separate volume), Kustannusosakeyhtiö Otavan kirjapaino, Helsinki, 1950.

ANNALS OF THE UNIVERSITY OF STELLENBOSCH. Volume 26, Section A, Nos. 3-11, 1950. Edited by C. A. DuTOIT. 507 pages. Price 1'1'0 (\$2.90). Cape Town, South Africa.

Volume 26 of the *Annals of the University of Stellenbosch* contains nine articles on the geology and petrology of South Africa. *Aspects of the Geology of the Northern Soutpansberg Area* by J. S. Van Zyl demonstrates that the Soutpansberg is a stepfault-block mountain-land and describes rocks of the Karro and Waterberg systems, the Old granite, the James-



town intrusives (anorthosites, perknites and serpentinites) and the Moodies series (quartzites, magnetite-quartz rocks, marbles and aluminous gneisses and schists). W. C. Brink, in *The Geology, Structure and Petrology of the Nuwerus Area, Cape Province*, depicts the geological features of an area underlain by rocks of the basement complex (Namaqualand granite with roof pendants of the Kaaieu series), of the Nama system and by a few diabase dikes. Deductions on the contamination of granite magna by country rock assimilation, based on the criteria of chemical analyses alone, are reviewed and criticized.

A new deposit of pyrophyllite, described by C. T. Potgieter in *The South African Pyrophyllite Deposits*, consists of a sericite schist containing kyanite, andalusite and diasporite as well as pyrophyllite. In the fourth paper, *The Geology and Chemistry of the Laingsburg Phosphorites*, H. C. Strydom presents a geologic and petrographic description of the Upper Dwyka shales and their phosphorite concretions and suggests a theory of origin. *The Dolerite Intrusions of the Wellington-Moorreesburg Area* by Q. C. Bouman concerns itself with the petrology of these rocks and the low-grade regional metamorphism responsible for their alteration. By means of grain-count and elongation-index-frequency methods, M. R. Henzen, in his paper, *A Comparative Petrographic Study of the Sediments of the Rooiberg and Stavoren-Vlakfontein Areas*, concludes that the quartzites of two separate occurrences had dissimilar provenances.

The second paper by C. T. Potgieter is entitled, *The Structure and Petrology of the George Granite Plutons and the Invaded Pre-Cape Sedimentary Rocks*, and deals with the petrography of the granite and of the country-rock schists, phyllites and quartzites. The next paper, *Morphological Aspects of the Bokkeveld Series at Wuppertal, Cape Province*, by B. Swart is concerned with the sedimentary structures, heavy minerals and fossils of these rocks. The last paper is by P. J. Van Zijl (spelled Zyl in the Table of Contents) on the petrography and petrogenesis of *The Complex Dioritic Stocks West of the Malmesbury-Paardeberg Granite Pluton*.

Throughout the volume the authors and editors have successfully maintained a high standard—in content, organization and presentation. Many large folded insert maps illustrate the reports.

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## NEW MINERAL NAMES

### Priderite

K. NORRISH, Priderite, a new mineral from the leucite-lamproites of the west Kimberley area, Western Australia: *Mineralog. Mag.*, **29**, 496-501 (1951).

CHEMICAL PROPERTIES: Analysis of 0.15 g. gave:  $\text{SiO}_2$  0.0,  $\text{TiO}_2$  70.6,  $\text{Fe}_2\text{O}_3$  12.4,  $\text{Al}_2\text{O}_3$  2.3,  $\text{BaO}$  6.7,  $\text{K}_2\text{O}$  5.6,  $\text{Na}_2\text{O}$  0.6,  $\text{CaO}$  trace,  $\text{MgO}$  0.0; sum 98.2% (analysis by the Assay Dept., School of Mines, South Australia, and J. D. Hayton). This corresponds to  $(\text{K}_{0.87}\text{Ba}_{0.32}\text{Na}_{0.14})(\text{Ti}_{6.48}\text{Fe}_{1.14}\text{Al}_{0.33})\text{O}_{16}$ . The mineral's x-ray diffraction pattern is unchanged after the mineral is heated to  $1400^\circ$ .

CRYSTALLOGRAPHIC PROPERTIES: Habit rectangular prisms with a lamellation parallel to the base. Cleavage basal, highly perfect and fair parallel to the prism. From powder data body-centered tetragonal with  $a = 10.11 \pm 0.02$  Å. ( $10.09\text{kX}$ ),  $c = 2.964 \pm 0.004$  Å. ( $2.958\text{kX}$ ); the unit cell contains approximately  $(\text{K}, \text{Ba})_{1.33}(\text{Ti}, \text{Fe})_8\text{O}_{16}$ . The x-ray pattern (data given) is very close to that of cryptomelane,  $(\text{KR}_8\text{O}_{16})$ ,  $\text{R} = \text{Mn}$  mainly). The structure must be a defect structure and the formula is generalized to  $\text{A}_{2-y}\text{B}_{8-z}\text{O}_{16}$ , with  $y$  approximately 1 and  $z$  very small.

PHYSICAL AND OPTICAL PROPERTIES: Color black, reddish. Luster adamantine. Streak gray. Occurs as rods about 0.05 mm. long, also as stout prisms up to  $1 \times 0.5$  mm.  $G. 3.86 \pm 0.08$  (micropyknometer). Optically positive with very high  $n$ ;  $\omega$  greater than 2.10. Pleochroic,  $\omega$  deep reddish-brown,  $\epsilon$  deep reddish-brown to black. Weakly attracted by an electromagnet. Closely resembles rutile, for which it was first mistaken.

SYNTHESIS: The K and Ba compounds were prepared by fusing mixtures of  $\text{TiO}_2$  with  $\text{K}_2\text{CO}_3$  or  $\text{BaCO}_3$  in an oxyacetylene flame, also by heating  $\text{KF} + \text{TiF}_4$  at  $1,000^\circ \text{C}$ .

OCCURRENCE: A characteristic accessory in all the leucite-bearing rocks of the area (Wade and Prider, *Quart. J. Geol. Soc. London*, **96**, 39-98 (1940)).

NAME: For Professor Rex Tregilgas Prider, Dept. Geology, University of Western Australia.

MICHAEL FLEISCHER

### Medmontite, Cupromontmorillonite

F. V. CHUKHROV AND F. YA. ANOSOV, Medmontite, a copper-bearing mineral of the montmorillonite group: *Zapiski Vsesoiuznoe Mineralog. Obshch.* (Mem. soc. russe mineral.), **79**, No. 1, 23-27 (1950); abstracted from a translation kindly made by Mr. V. L. Skitsky.

This clay mineral occurs in the upper part of the oxidation zone of the Dzhzhkazgan copper deposits, Kazakhstan, U.S.S.R. It is in compact aggregates gray to pinkish.  $H. = 2\frac{1}{2}$ ,  $G. = 2.49-2.53$ . Fracture uneven to conchoidal. Adheres to the tongue. Under the microscope, it shows leaflets with mean  $n = 1.572$ . When heated the clay turns black; after being heated to  $500^\circ$ , its  $n = 1.590$ . Analysis gave:  $\text{SiO}_2$  43.88,  $\text{TiO}_2$  0.72,  $\text{Al}_2\text{O}_3$  13.25,  $\text{Fe}_2\text{O}_3$  3.25,  $\text{CuO}$  20.96,  $\text{MgO}$  0.59,  $\text{MnO}$  0.06,  $\text{CaO}$  1.58,  $\text{Na}_2\text{O}$  0.44,  $\text{K}_2\text{O}$  0.87,  $\text{H}_2\text{O} - 7.02$ ,  $\text{H}_2\text{O} + 7.52$ ; sum 100.14%. This gives  $\text{Cu}_{1.33}\text{Mg}_{0.08}\text{Al}_{1.04}(\text{Al}_{0.28}\text{Si}_{3.72})\text{O}_{10}(\text{OH})_2\text{X}_{0.33}$  in the Ross-Hendricks' formulation, where X is exchangeable cations (K, Na, Ca). X-ray data show the mineral to be a member of the montmorillonite group. Differential thermal analysis shows peaks at 140, 570, and  $800^\circ \text{C}$ . Like montmorillonite, the mineral absorbs much water (up to 49% in 136 hours) and loses it readily on exposure to a drier atmosphere. Very little Cu was leached by treatment with concentrated ammonia.

NAME: Apparently coined from mede (=copper) and montmorillonite.

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**Nogizawalite**

TEIKICHI KAWAI, On nogizawalite, a new mineral found near Ishikawa, Fukushima Prefecture (Japan): *J. Chem. Soc. Japan* (Pure Chemistry Section) **70**, 268-270 (1949). Abstracted from a translation by Skigeo Ofuji, edited by Miss Rachel Barker, U. S. Geological Survey, Tokyo.

The name, for one of the areas (Nogizawa-mura) in which the material was found, is given to a fine-grained aggregate shown by x-ray study to contain xenotime and zircon. Apatite may be present and the presence of other minerals is suggested by the low specific gravity, 3.42, and the analysis, which gave: MgO 4.47, CaO 14.01, FeO 3.00, Fe<sub>2</sub>O<sub>3</sub> 10.08, Al<sub>2</sub>O<sub>3</sub> 10.55, rare earths 25.99, SiO<sub>2</sub> 15.09, ZrO<sub>2</sub> 4.55, P<sub>2</sub>O<sub>5</sub> 9.78, H<sub>2</sub>O 2.52; sum 100.04%. Occurs in several pegmatites.

DISCUSSION: Kawai states, "It does not form a new species in a rigorous sense of mineralogy, as it is an aggregate consisting of two or more species. However, it is reasonable that a new name should be given to the mineral since these constituents are so closely connected that they are inseparable, and this aggregate is not formed accidentally, but fixed."

The reasons given are not valid and names like this one are useless.

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